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A Thermodynamic Study on the Complex Formation Between Tris(2-Pyridyl)Methylamine (tpm) with Fe^{2+}, Fe^{3+}, Cu^{2+} and Cr^{3+} Cations in Water–Acetonitrile Binary Solutions Using the Conductometric Method

Majid Rezayi[1,2*], *Lee Yook Heng*[2*], *Mahnaz M. Abdi*[3], *Norfadila MD Noran*[3], *Chakavak Esmaeili*[2], *Seyedeh Belin Tavakoly Sany*[1,4], *Aishah Salleh*[4], *Leila Narimani*[2], *Naghmeh saadati*[2], *Faezeh Tajalli*[1]

[1] Food Science and Technology Research Institute, ACECR Mashhad Branch, Mashhad, Iran.
[2] School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor D.E., Malaysia.
[3] Department of Chemistry Faculty of Sciences, Universiti Putra Malaysia, 43400 Serdang, Selangor D.E., Malaysia.
[4] Institute of Biological Sciences University of Malaya, 50603 Kuala Lumpur, Malaysia.
[*]E-mail: chem_rezayi@yahoo.com; leeyookheng@yahoo.co.uk

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The complexation reactions between tris(2pyridyl) methylamine, tpm with Cu^{2+}, Fe^{2+}, Fe^{3+} and Cr^{3+}, cations, were examined in acetonitrile-water (AN–H_2O) binary mixtures. This research has been studied at different temperatures (15, 25 and 35 °C) by applying conductometric method. In all cases, tpm forms 1:1 complexes with these cations. The stability constant of the complexes were obtained from fitting the molar conductivity curves using a computer program, Genplot. The non-linear behavior which was discovered for variations of log K_f of the complexes versus the composition of the mixed solvents was discussed in terms of changing the chemical and physical properties of the constituent solvents when they mix with one another. The values of thermodynamic parameters, standard enthalpy (ΔH_c^o) and standard entropy (ΔS_c^o) for formation of the complexes were obtained from temperature dependence of the stability constants using the van't Hoff plot. The results show that the complexes are both enthalpy and entropy stabilized. The selectivity order of the tpm towards metal cations at 25°C in pure H_2O is: (tpm–Cr^{3+}) > (tpm–Fe^{2+}) > (tpm–Cu^{2+}) > (tpm–Fe^{3+}). However, the selectivity order of the tpm towards metal cations at 25°C in mol% AN = 34.08 is: (tpm–Cr^{3+}) > (tpm–Fe^{3+}) > (tpm–Fe^{2+}) > (tpm–Cu^{2+}). In conclusion, the selectivity order for all complexes are changing as well as the composition of the solvent mixtures also changed.

Keywords: tris(2pyridyl) methylamine, conductometric method, acetonitrile-water, van't Hoff plot.

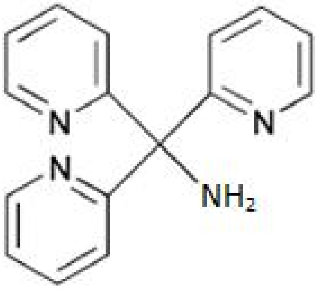
1. INTRODUCTION

Macrocylic compounds occupy an important place in chemistry. A macrocyclic compounds can be defined as a polydentate ligand, with donor atoms attached to a cyclic backbone. According to host–guest chemistry, macrocyclic compounds have the capability of forming complexes with alkalis and alkaline earth metal ions through electrostatic attraction and encapsulation in the macrocyclic cavity [1]. The concept of host–guest chemistry is related to supramolecular chemistry, which is a study about non-covalent forces and the structures created by these forces. This has been inspired by biology and built on the back of synthetic organic chemistry and inorganic co-ordination chemistry.

Much research has been done on this macrocylic compound, as it provides us with many chemical opportunities. There have been many papers where chemists have reported applications such as in the construction of ion-selective electrodes [2, 3], membrane separation processes [4], fiber optic chemical sensors [5], chiral separation [6], pre-concentration of metal ions [7] and phase transfer catalysts [8]. As a consequence, all of these applications have provided more benefits and developed more branches in the world of chemistry and in the study of these macrocylic compounds.

Recently, there has been, much research on complex formation. There are a number of physico-chemical techniques that can be used in the study of these complexation reactions, for example, spectrophotometry, polarography, NMR spectrometry, calorimetry, potentiometry and conductometry [9]. Nevertheless of all these techniques, conductometric techniques are the most useful for studying this complexation of complexes. This is because conductometric techniques are highly sensitive and inexpensive, with a simple design of experimental arrangement for such investigations [10]. Therefore, it offers more benefits than the other methods.

In this study, we discuss the complexation reaction between tpm that acts as a ligand with Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} cations in acetonitrile–water (AN–H_2O) binary mixtures at different temperatures (15, 25 and 35^{o}C). This study has been conducted at different temperatures by applying the conductometric method. Consequently, we will study the effect of solvent properties, AN–H_2O as well as the effect of composition of the binary mixed solvents on stoichiometry and the selectivity between ligand and ions in various systems.



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

Tpm is an example of tripodal ligands, based on nitrogen heterocycles. The co-ordination chemistry of this tripodal ligand, tpm, with copper (I), copper (II) and zinc (II) has been studied. The synthesis of tpm can readily be modified to approach a variety of related tripodal ligands, such as 2-(methylsulfanyl)-1 and 1-di(2 pyridyl)ethylamine (MDE). Moreover, the primary amine function can be derived further in order to extend the range of complexes obtained [11].

In this research, we have used a mixture of the two solvents, AN–H_2O, since mixed solvents play an important role in this branch of chemistry.

2. EXPERIMENTAL

2.1. Reagents

Chromic(III)nitrate (BDH Chemical & LTD Poole England), copper(II)chloride-2-hydrate (Hamburg) , ferum (II) chloride-4-hydrate and ferum(III)chloride (Merck) were used without further purification. Acetone, acetonitrile (Ajax) of the highest purity and deionized distilled water were used as solvents. The tpm was synthesized and purified by the organic chemistry group in UPM and then used.

2.2. Apparatus

In this research, the digital Hanna conductivity apparatus (Model HI 255) was used. This instrument was connected to the thermostatted water bath and the temperature was kept constant during the experiment to within $\pm 0.01^{\circ}C$. The cell comprising two platinum electrodes was used in order to evaluate the electrolytic conductance, which the alternating potential applied. A conductometric cell with a cell constant of 0.99 cm^{-1} was used throughout the studies. By using a standard solution of KCl (0.1000 M), the cell was calibrated every time before use.

2.3. Methodology

In this study, two types of solution were prepared: a cation salt solution and the ligand, tpm solution. 25 ml cation salt solution chromium(III) nitrate, copper(II)chloride-2-hydrate, iron(II) chloride-4-hydrate and iron(III) chloride) with a concentration of 5.0×10^{-5} M were placed in the water-jacketed cell, which contained a magnetic stirrer. The speed of stirring was constant for each experiment. This water-jacketed cell was connected to the circulating water in order to maintain the temperature. Then, the known amount of the ligand, tpm solution with a concentration of 2.5×10^{-3} M was added, using a micropipette. The conductance value was assessed after each addition of ligand. The addition of the ligand was continuous, until the desired ligand-to-cation mole ratios were achieved. A Genplot computer program was used to record the variations of stability constant, log $K_{f.}$ between the ligand, tpm and the chosen metal cations.

3. RESULTS

The purpose of this study is to investigate the change of molar conductance (Λ_m) with the ligand to cation mole ratio, ($[L]_t/[M]_t$) for the complex formation of tpm with Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} cations. This research was conducted in acetonitrile–water (AN–H_2O) binary mixtures at different temperatures (15, 25 and 35°C), using the conductometric method. The molar conductance, (Λ_m) was evaluated in pure AN, H_2O and in AN–H_2O binary mixtures at different temperatures. $[L]_t$ is the total concentration of the ligand (tpm), while $[M]_t$ is the total concentration of the Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} metal cations. Two typical series of molar conductance values as a function of ($[L]_t / [M]_t$) for (tpm–Cr^{3+}) and (tpm–Cu^{2+}) in AN–H_2O binary solutions are shown in Figs. 1 and 2, respectively.

Table 1 presents the log K_f values of the complexes formed at different temperatures between tpm and Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} cations in pure AN and H_2O and AN–H_2O binary mixtures at different temperatures by applying the conductometric method. The calculated thermodynamic parameters (ΔH_C^{O}, ΔS_C^{O} and ΔG_C^{O}) were obtained from the variations of molar conductance as a function of the ($[L]_t / [M]_t$) mole ratio, using a computer program, Genplot [12]. All of these calculated thermodynamic parameters at 25°C for tpm–Cr^{3+}, tpm–Cu^{2+}, tpm–Fe^{2+} and tpm–Fe^{3+} complexes in pure AN, H_2O and AN–H_2O binary mixtures are summarized in Table 2.

The changes in stability constant (log K_f) for complex formation with the composition of AN–H_2O binary systems at different temperatures have been established in Fig 3. The van’t Hoff plots of LnK_f against 1/T have been shaped for all the investigated systems as demonstrated in Fig 4. The value of enthalpy changes, ΔH_C^{O} is obtained from the plots of van’t Hoff, while the entropy changes, ΔS_C^{O} are determined from the following equation: $\Delta G^{O}_{C,298.15} = \Delta H_C^{O} - 298.15\ \Delta S_C^{O}$ [13]. The changes in stability constant (log K_f) of the complexation reactions against cationic radii in various solvent systems at 25°C are shown in Fig 5.

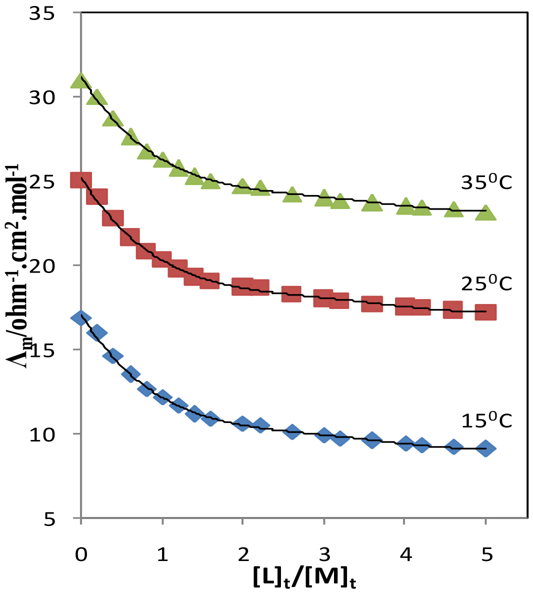


Figure 1. Molar conductance mole-ratio plot for the (tpm–Cr^{3+}) complex in AN–H_2O binary system (mole% AN= 92.07) at different temperatures

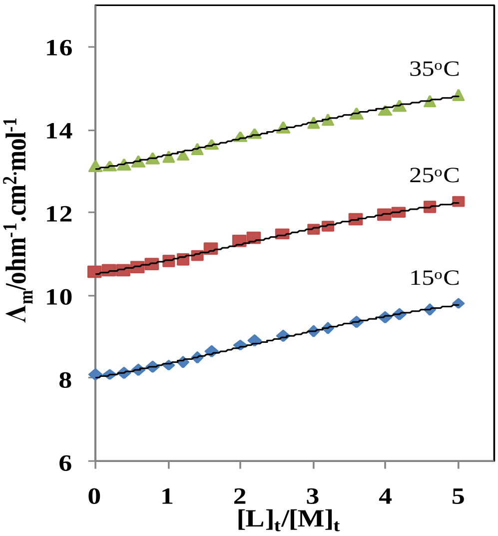


Figure 2. Molar conductance mole-ratio plot for the (tpm–Cu^{2+}) complex in AN–H_2O binary system (mole% AN= 65.92) at different temperatures

Table 1. Log K_f values of tpm-Cr^{3+}, tpm–Cu^{2+}, tpm-Fe^{2+} and tpm–Fe^{3+} in AN–H_2O binary mixtures at different temperatures

Medium	Log K_f ± SD[a]		
	15°C	25°C	35°C
tpm-Cr^{3+}			
Pure AN	3.22 ± 0.20	3.18 ± 0.22	3.16 ± 0.04
57.96%AN-42.04% H_2O[b]	3.31 ± 0.15	3.31 ± 0.15	3.30 ± 0.16
34.08% AN-65.92% H_2O	3.69 ± 0.09	3.70 ± 0.09	3.72 ± 0.09
18.69% AN-81.31% H_2O	3.84 ± 0.11	3.84 ± 0.11	3.85 ± 0.11
7.93% AN-92.07% H_2O	4.67 ± 0.04	4.68 ± 0.04	4.68 ± 0.04
Pure H_2O	3.20 ± 0.30	3.23 ± 0.26	3.24 ± 0.25
tpm-Cu^{2+}			
Pure AN	2.60 ± 0.22	2.62 ± 0.20	2.63 ± 0.20
57.96% AN-42.04% H_2O	2.85 ± 0.25	2.86 ± 0.25	2.87 ± 0.26
34.08% AN-65.92% H_2O	2.66 ± 0.36	2.65 ± 0.35	2.64 ± 0.34
18.69% AN-81.31% H_2O	2.79 ± 0.34	2.81 ± 0.32	2.82 ± 0.30
7.93% AN-92.07% H_2O	2.86 ± 0.30	2.86 ± 0.30	2.87 ± 0.30
Pure H_2O	2.87 ± 0.24	2.78 ± 0.26	2.77 ± 0.26
tpm-Fe^{2+}			
Pure AN	2.86 ± 0.29	2.87 ± 0.29	2.87 ± 0.29
57.96% AN-42.04% H_2O	2.85 ± 0.25	2.86 ± 0.25	2.87 ± 0.25
34.08% AN-65.92% H_2O	2.88 ± 0.31	2.87 ± 0.32	2.82 ± 0.35
18.69% AN-81.31% H_2O	2.44 ± 0.30	2.42 ± 0.29	2.40 ± 0.30
7.93% AN-92.07% H_2O	2.79 ± 0.33	2.80 ± 0.34	2.80 ± 0.35
Pure H_2O	2.85 ± 0.31	2.85 ± 0.31	2.84 ± 0.32
tpm-Fe^{3+}			
Pure AN	2.87 ± 0.32	2.87 ± 0.31	2.86 ± 0.32
57.96% AN-42.04% H_2O	2.72 ± 0.36	2.75 ± 0.35	2.75 ± 0.34
34.08% AN-65.92% H_2O	3.50 ± 0.11	3.40 ± 0.10	3.49 ± 0.10
18.69% AN-81.31% H_2O	3.16 ± 0.35	3.16 ± 0.35	3.15 ± 0.36
7.93% AN-92.07% H_2O	2.92 ± 0.24	2.92 ± 0.23	2.93 ± 0.25
Pure H_2O	2.59 ± 0.34	2.65 ± 0.30	2.64 ± 0.30

[a] SD= standard deviation.

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

Table 2. Thermodynamic parameters for tpm–Cr^{3+}, tpm–Cu^{2+}, tpm–Fe^{2+} and tpm–Fe^{3+} in AN–H_2O binary mixtures at different temperatures

Medium	$-\Delta G_C^O \pm SD^a$ kj/mol	$\Delta H_C^O \pm SD^a$ kj/mol	$\Delta S_C^O \pm SD^a$ $j/mol°K$
tpm-Cr^{3+}			
Pure AN	18.14 ± 1.28	-5.25 ± 1.25	43.47 ± 0.87
57.96%AN-42.04% H_2O^b	18.87 ± 0.90	-0.96 ± 0.02	60.07 ± 3.02
34.08% AN-65.92% H_2O	21.13 ± 0.55	0.10 ± 0.07	71.21 ± 1.85
18.69% AN-81.31% H_2O	21.89 ± 0.63	-0.10 ± 0.03	73.09 ± 2.10
7.93% AN-92.07% H_2O	26.69 ± 0.26	0.70 ± 0.42	91.87 ± 1.11
Pure H_2O	18.44 ± 1.49	2.92 ± 0.78	71.64 ± 4.26
tpm-Cu^{2+}			
Pure AN	14.96 ± 1.16	1.31 ± 0.40	54.57 ± 3.65
57.96% AN-42.04% H_2O	16.33 ± 0.03	0.26 ± 0.02	55.65 ± 0.05
34.08% AN-65.92% H_2O	15.10 ± 2.02	-1.03 ± 0.06	47.22 ± 6.77
18.69% AN-81.31% H_2O	16.01 ± 1.84	2.37 ± 0.12	61.64 ± 6.15
7.93% AN-92.07% H_2O	16.32 ± 1.74	-0.92 ± 0.40	51.65 ± 5.67
Pure H_2O	15.85 ± 1.47	-8.31 ± 4.49	25.28 ± 4.49
tpm-Fe^{2+}			
Pure AN	16.37 ± 1.41	0.50 ± 0.12	56.58 ± 4.73
57.96% AN-42.04% H_2O	16.31 ± 1.67	0.84 ± 0.03	57.50 ± 5.60
34.08% AN-65.92% H_2O	16.41 ± 1.82	-5.36 ± 2.73	37.06 ± 6.82
18.69% AN-81.31% H_2O	13.82 ± 1.66	-2.54 ± 0.32	37.83 ± 5.46
7.93% AN-92.07% H_2O	15.96 ± 1.79	1.23 ± 0.02	57.64 ± 6.00
Pure H_2O	16.28 ± 1.83	-0.25 ± 0.12	53.79 ± 6.11
tpm-Fe^{3+}			
Pure AN	16.37 ± 1.79	0.65 ± 0.22	57.09 ± 5.59
57.96% AN-42.04% H_2O	15.71 ± 2.00	2.18 ± 0.98	60.00 ± 5.84
34.08% AN-65.92% H_2O	19.91 ± 0.59	-1.38 ± 0.39	62.15 ± 1.47
18.69% AN-81.31% H_2O	18.03 ± 2.00	0.19 ± 0.06	61.12 ± 6.70
7.93% AN-92.07% H_2O	16.70 ± 1.34	0.67 ± 0.04	58.25 ± 4.50
Pure H_2O	15.11 ± 1.68	1.31 ± 0.40	55.07 ± 5.42

[a] SD= standard deviation.

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

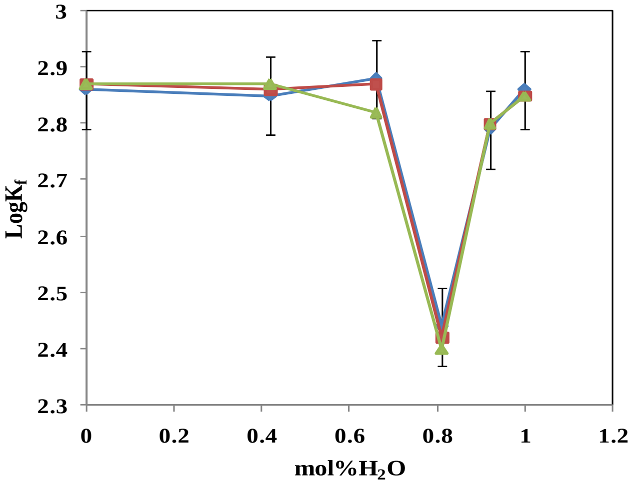


Figure 3. Changes of the stability constant (log K_f) of (tpm–Fe^{2+}) complex with the composition of AN–H_2O binary systems at different temperatures: (● 15^OC, ■ 25^OC, ▲ 35^OC)

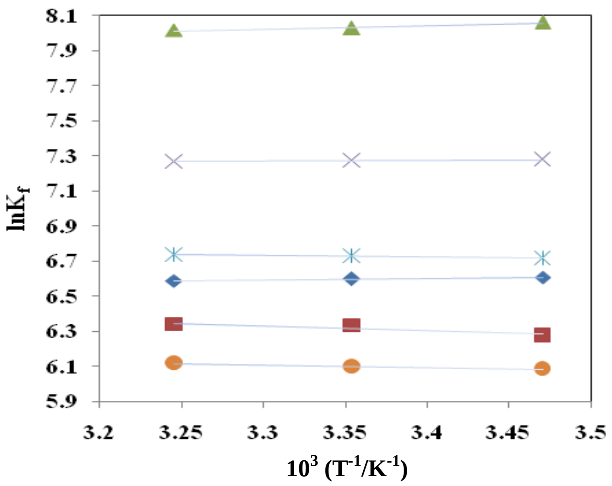


Figure 4. Van't Hoff plots for (tpm–Fe^{3+}) complex in AN–H_2O binary systems: (mol% AN: ♦100, ■57.96, ▲34.08, x 18.69, *7.93, ● 0.00)

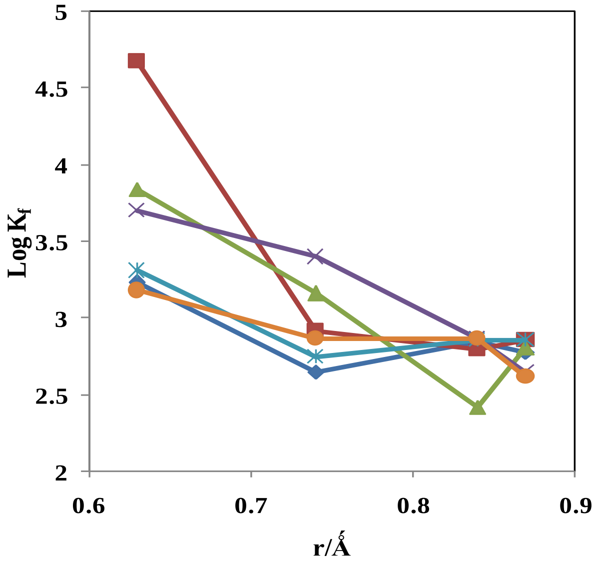


Figure 5. Changes of the stability constant (log K_f) for (tpm–Cr^{3+}), (tpm–Cu^{2+}), (tpm–Fe^{2+}) and (tpm–Fe^{3+}) complexes versus cationic radii in various solvent systems at 25°C: (mol% AN: ♦ 0.00, ■ 7.93, ▲18.69, x 34.08, * 57.96 ●100)

4. DISCUSSION

Figure 1 shows the stability constants of the complexes that are computed by conductometrry of a binary mixture of AN–H_2O at different temperatures. Figure 1 presents a gradual decrease in molar conductivity with an increase in ligand concentration. This suggests that the tpm–Cr^{3+} is less mobile than the free solvated Cr^{3+} cation. In addition, it appears that the Cr^{3+} cation is more weakly solvated by the solvent molecules [14]. The gradient of the slope representing molar conductivity against ligand to cation mole ratio plots varies at the point where the ratio is about 1, which demonstrates the formation of a 1:1 [M:L] complex in solution [15, 16].

However, as demonstrated in Fig 2, the addition of the tpm ligand to the Cu^{2+} cation in AN–H_2O binary mixtures at different temperatures raises the molar conductivity, (Λ_m) values with raised tpm/Cu^{2+}. This behaviour indicates that the tpm–Cu^{2+} complex in these systems has a higher mobility than the free solvated Cu^{2+} cation. This indicates that the Cu^{2+} cation is stronger solvated by the solvent molecules. The gradient of molar conductivity against ligand to cation mole ratio plots varies at the point where the ratio is about 1, introducing the 1:1 [M:L] complex in solutions.

For the tpm–Cr^{3+} and tpm–Cu^{2+} complexes, the stability constant of the complexes increases with the temperature in most solvent systems [17], which is presented in Table 1. This indicates that both complexes have experienced an endothermic complexation reaction between the ligand and the ions in the solutions. Thus, it can be stated that the nature of the solvent has a fundamental effect on the stability of the resulting complexes [18]. However, for the other two complexes: tpm–Fe^{2+} and tpm–Fe^{3+}, the stability constants of the complexes show a decrease with increased temperature in most solvent systems. This indicates that the complexation processes for both these complexes are exothermic.

Table 1 has shown that the value of the stability constant increases with increasing mol% of water in the AN–H_2O binary mixtures for tpm–Cu^{2+}. The outcome is preferable to the interactions between tpm and the AN molecules, which involves hydrogen bonding between CH_3 protons, and the AN involves nitrogens in tpm. In addition, the Cu^{2+} cation, as a soft acid, will interact with the nitrogen atom of the acetonitrile molecule as a soft base. Thus, the Cu^{2+} cation is solvated to a higher extent in an AN solvent. The same conditions also apply to the stability constant of the tpm–Cr^{3+} complex.

Most of the cases in the tpm–Fe^{2+} complex show an increase in stability constant with a decrease in the mol% of water in the AN–H_2O binary mixtures. In water with a high Gutmann Donor Number (DN = 18.0), the solvation of the Fe^{2+} cation should be stronger than in acetonitrile with a lower solvating ability (DN = 14.1) [19]. There is actually an inverse relationship between the stabilities of the complexes and the solvating abilities of the solvents [20]. Therefore, the stability constant of the tpm–Fe^{2+} complex increases as the concentration of water is lowered in AN–H_2O binary mixtures.

As expressed in Table 1, the stability constant of the tpm–Fe^{3+} complex shows an increase in most cases, with a decrease in the mol% of water in the AN–H_2O binary mixtures. As conveyed by the Gutmann Donor Number, in solvents with a low DN, the cation and ligand are poorly solvated and can easily be complexed [21]. In this research, acetonitrile has a low donor number compared with the water. Therefore, water has a higher ability to solvate the Fe^{3+} cation. Again, the stability constant of the tpm–Fe^{3+} complex increases as the concentration of water is lowered in AN–H_2O binary mixtures, which varies inversely with the Gutmann Donicities.

The thermodynamics of the complex formation of tpm with Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} cations is dependent on the nature and composition of the mixed solvents as expressed by the result of calculated standard enthalpy, (ΔH_C^{O}) and standard entropy, (ΔS_C^{O}) from Table 2. The complexes in most cases are enthalpy and entropy stabilized [22]. Since the reactions are enthalpy and entropy stabilized, it can stated that both the enthalpy and entropy of the complexation reactions are the principal driving forces for the formation of these complexes in most solvent systems [23].

From Fig 3, the experimental values of ΔH_C^{O} and ΔS_C^{O} established that the enthalpies and entropies of the (tpm–Fe^{2+}) complex versus the composition of the AN–H_2O binary system at respective temperatures do not deviate monotonically with the solvent composition. This behaviour possibly reflects the strong interactions between the component solvent molecules, which result in changes to some of the chemical and physical properties of each of the solvents, therefore, altering their solvating powers towards the dissolved species. In addition, the heteroselective solvation of the cation causes its character to alter with the composition of the mixed solvent,.and temperature may be efficient in the complexation reactions. Besides, there are many factors that affect the enthalpies and entropies of complexation reactions. Hence, a monotonic relationship within these thermodynamic evaluations and the solvent composition of the binary mixtures of these two dipolar protic and aprotic solvents should not be assumed [24].

The van't Hoff plots of LnK_f versus 1/T for all complexes systems have been shaped. The distinctive example of these diagrams for the tpm–Fe^{3+} complex in pure AN, H_2O and in AN–H_2O binary systems are depicted in Fig 4. The enthalpies and entropies of complexation were extrapolated in the usual manner from the slopes and intercepts of the plots [25]. The results of the enthalpies and entropies are also included in Table 2.

Figure 5 expresses the changes in the stability constant (log K_f) for the complex formation of tpm–Cr^{3+}, tpm–Cu^{2+}, tpm–Fe^{2+} and tpm–Fe^{3+} against the cationic radii in pure AN, H_2O and binary mixtures of AN–H_2O. According to Fig 5, the selectivity of tpm towards Cr^{3+}, Cu^{2+}, Fe^{2+} and Fe^{3+} changes as the mol% of H_2O in the binary mixtures changes. This can be explained in terms of the properties of the mixed solvents. When two different mixtures of solvent with their different compositions are mixed, their physical and chemical properties will change. Therefore, each different composition of the AN–H_2O binary mixture results in a different order of selectivity. This can be proved from Fig 5. The selectivity order of the tpm towards metal cations at 25°C in pure H_2O is: (tpm–Cr^{3+}) > (tpm–Fe^{2+}) > (tpm–Cu^{2+}) > (tpm–Fe^{3+}). However, the selectivity order of the tpm towards metal cations at 25°C in mol% AN = 34.08 is: (tpm–Cr^{3+}) > (tpm–Fe^{3+}) > (tpm–Fe^{2+}) > (tpm–Cu^{2+}).

5. CONCLUSION

This research focused on the study of thermodynamic complexation reactions between the ligand, tpm, with chromium(III), copper(II), iron(II) and iron(III) metal cations. The stability constants of the complex formation between ligand and metal cations was investigated by applying the conductometric method at different temperatures.

Based on the results, the stability constant (at identical temperatures) for the complexation reaction of tpm–Cr^{3+} and tpm–Cu^{2+} shows an increase with an increasing water percentage in these solvent systems, while, the formation constant of tpm–Fe^{2+} and tpm–Fe^{3+} shows a decrease with increasing water percentage in (AN–H_2O) binary systems.

In this thermodynamic study, the negative sign of the ΔG_C^{O} shows that the ligand is capable of forming stable complexes and that the process will proceeding spontaneously, while the positive sign of the entropy shows that ΔS_C^{O} is the driving force of the complexation reaction in this complex formation. These facts mean that ΔG_C^{O} is always negative and ΔS_C^{O} is always positive.

A 1:1 complex formation has been obtained for these four complexes in all their systems. The factor in determining the selectivity order for these complexes, such as radii of metal cations plays an important role which has been depicted in Fig 5. The selectivity order for all these complexes changes when the composition of the mixed solvents changes. This is due to the changing of physical and chemical properties of the two different solvents when they are mixed together. In conclusion, this research can be used for the fabrication of an ion selective electrode to determine the chromate ion.

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References

1. G.H. Rounaghi, M. Mohajeri, S. Ahmadzadeh, and S. Tarahomi, *J. Inclusion Phenom. Macrocyclic Chem*, 63 (2009) 365-372.
2. A. Kassim, M. Rezayi, S. AhmadZadeh, W.T. Tan, N.A. Yusof, and L.Y. Heng, *Malaysian Journal of Chemistry*, 11 (2009) 019-025.
3. A. Kassim, M. Rezayi, S. Ahmadzadeh, G. Rounaghi, M. Mohajeri, N.A. Yusof, T.W. Tee, L.Y. Heng, and A.H. Abdullah. *A Novel ion selective polymeric membrane sensor for determining thallium (I) with high selectivity*. in *IOP Conference Series: Materials Science and Engineering*. IOP Publishing.
4. N. Rawat, P.K. Mohapatra, D.S. Lakshmi, A. Bhattacharyya, and V.K. Manchanda, *J Membrane Sci*, 275 (2006) 82-88.
5. N. Malcik, N. Tunoglu, P. Caglar, and G.E. Wnek, *Sensors Actuat B-Chem*, 53 (1998) 204-210.
6. S. Seyhan, Y. Turgut, M. Merdivan, and H. Hosgören, *Tetrahedron: Asymmetry*, 17 (2006) 1700-1704.
7. B. Saad, C.C. Chong, A.S.M. Ali, M.F. Bari, I.A. Rahman, N. Mohamad, and M.I. Saleh, *Anal Chim Acta*, 555 (2006) 146-156.
8. N. Jose, S. Sengupta, and J.K. Basu, *J Mol Catal A-Chem*, 309 (2009) 153-158.
9. M. Rezayi, S. Ahmadzadeh, A. Kassim, and Y.H. Lee, *Int J Electrochem Sci*, 6 6350-6359.
10. G.H. Rounaghi and F. Mofazzeli, *J. Inclusion Phenom. Macrocyclic Chem*, 51 (2005) 205-210.
11. P.J. Arnold, S.C. Davies, J.R. Dilworth, M.C. Durrant, D.V. Griffiths, D.L. Hughes, R.L. Richards, and P.C. Sharpe, *J. Chem. Soc., Dalton Trans.*, (2001) 736-746.
12. S. Ahmadzadeh, A. Kassim, M. Rezayi, and G.H. Rounaghi, *Molecules*, 16 8130-8142.
13. G.H. Rounaghi, M.H.A. Zavvar, F. Boosaeedi, and R.S. Khoshnood, *J. Inclusion Phenom. Macrocyclic Chem*, 47 (2003) 101-107.
14. G.H. Rounaghi and E. Razavipanah, *J. Inclusion Phenom. Macrocyclic Chem*, 61 (2008) 313-318.
15. G. Ronagi, *J. Inclusion Phenom. Macrocyclic Chem*, (2009)
16. M. Rezayi, A. Kassim, S. Ahmadzadeh, A. Naji, and H.A. Ahangar, *Int J Electrochem Sci*, 6 4378-4387.

17. M. Joshaghani, M.B. Gholivand, and F. Ahmadi, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 70 (2008) 1073-1078.
18. M. Hasani and M. Shamsipur, *J. Inclusion Phenom. Macrocyclic Chem*, 16 (1993) 123-137.
19. G.H. Rounaghi, M.H.A. Zavvar, K. Badiee, F. Boosaidi, and M.S. Kazemi, *J. Inclusion Phenom. Macrocyclic Chem*, 59 (2007) 363-369.
20. G. Rounaghi, Z. Eshaghi, and E. Ghiamati, *Talanta*, 44 (1997) 275-282.
21. G.H. Rounaghi, R.S. Khoshnood, and M.H.A. Zavvar, *J. Inclusion Phenom. Macrocyclic Chem*, 54 (2006) 247-252.
22. G. Khayatian, S. Shariati, and M. Shamsipur, *J. Inclusion Phenom. Macrocyclic Chem*, 45 (2003) 117-121.
23. M. Shamsipur and M. Saeidi, *J Solution Chem*, 29 (2000) 1187-1198.
24. M. Shamsipur and G. Khayatian, *J. Inclusion Phenom. Macrocyclic Chem*, 39 (2001) 109-113.
25. A. Chatterjee, S.P. Moulik, S.K. Sanyal, B.K. Mishra, and P.M. Puri, *J Phys Chem-B*, 105 (2001) 12823-12831