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Interaction of Thallium (I) with Cytidine 5′-Monophosphate in Different Ionic Strengths and Various Media

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ABSTRACT

The formation constants of the species formed in the systems H^+ + cytidine 5′-monophosphate (CMP) and H^+ + cytidine 5′-monophosphate + Tl (I) ion have been determined in aqueous solution in a wide pH range of 1.5 to 10.5 at 25 °C and different ionic strengths ranging from 0.1 to 1.5 moldm^{-3} $NaClO_4$, $NaNO_3$, and NaCl using potentiometric-spectrophotometric technique. The composition of the complexes was specified and was shown that thallium ion forms mononuclear two 1:1 complexes with CMP. The general trend for the protonation constants of CMP and its complexes with thallium (I) are in the order of $NaClO_4$> $NaNO_3$> NaCl in different ionic media. The dependence of formation constants on ionic strength are described by a Debye-Huckel type equation and interpreted for the various supporting electrolytes.

Keywords: CMP; Tl(I); Protonation and complexation constants; Ionic strength; Salt effect

INTRODUCTION

Thallium and its salts are extremely toxic. Thallium ion can penetrate into the body through the skin, the lungs or when eaten with food [1-2]. The water soluble salts of thallium, such as thallium sulfate, are the most toxic and when absorbed in the body causes physiological damage rapidly. Thallium oxide, sulfide and metallic thallium are still very toxic but much less toxic than soluble thallium salts [3]. The toxicity of thallium ion is mainly due to the fact that the mono-valent thallium ion properties are very similar to the common potassium and sodium ions [4]. Since the size of the thallium ion is very close to that of the potassium ion, certain biochemical mechanisms in the body cannot distinguish between the two, and incorporate thallium instead of potassium when available [5]. Thus, biochemical mechanisms which require potassium ions, such as certain transmission of nervous messages, cannot be performed when thallium is incorporated instead of potassium [6]. The lethal dose for humans is 15-20 mg/kg, although smaller doses have also led to death [7-8]. Non-lethal doses cause toxic effects. Chronic thallium poisoning occurs over months or years of exposure to thallium.

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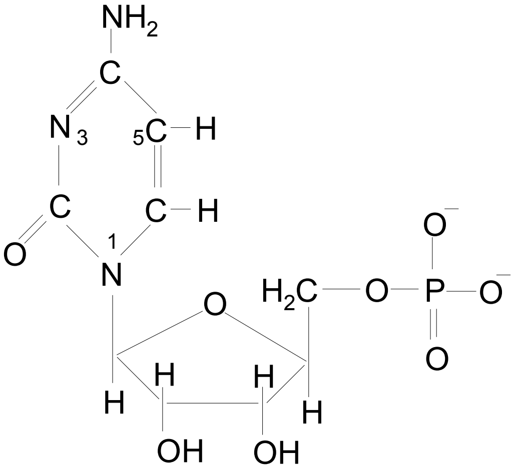
The absorbed thallium ion through the skin, respiratory, and gastrointestinal tracts can build up over some months or even years to reach the toxic level [9]. Because the presentation of chronic thallium poisoning appears similar to other diseases, many cases of industrial thallium exposure may go undetected. Signs and symptoms of chronic poisoning include tiredness, headaches, depression, hallucinations, psychosis, dementia, poor appetite, leg pains, hair loss and disturbances of vision. Therefore, it is interesting to study the interaction of Tl^+ ion with biological ligands such as nucleotides.

On the ionic strength dependence of formation constants for stable complexes of some amino acids, peptides, nucleosides, and nucleotides by some metal ions, we have reported some interesting features of the function log $K = f(I)$ [10-15], where K and I refer to formation constant and ionic strength, respectively. In particular, all the formation constants seem to follow the same trend as a function of ionic strength, if allowance is made for different types of reaction stoichiometry and different charges of reactants and products. In determining a formation constant at a fixed ionic strength, in all cases, some uncertainties are always present. This fact is mainly due to the uncertainties in the numerical values of formation constants. For example, up to 0.8 and 0.7 in log unit differences in the stability constants of the species MHL and ML, respectively, determined between 0.1 and 0.7 $moldm^{-3}$ should be the result of the uncertainties in the numerical values.

The present work deals with study of the H+ + CMP and Tl (I) + H+ + CMP systems in an ionic strength range of 0.1–1.5 moldm-3 sodium perchlorate, sodium nitrate, and sodium chloride as background electrolyte. The parameters which define the dependency were analyzed with the aim of obtaining further information with regard to their variation as a function of charges involved in the protonation of CMP and its complexation with thallium (I). Moreover, a Debye-Huckel type equation was established for the dependence of the formation constant on ionic strength.



Scheme 1. Chemical structure of CMP^{2-}.

EXPERIMENTAL

Chemicals

CMP, Scheme 1, was obtained from Fluka as analytical reagent grade material and used without further purification. Sodium perchlorate and sodium nitrate (from Merck) were dried under vacuum at room temperature for at least 72 hours before use. Sodium chloride (from Merck) was dried in an oven at 110 °C at least for 4 h. Perchloric, nitric and hydrochloric acids and thallium nitrate were all from Merck and were used as supplied. Sodium hydroxide solution, prepared from concentrated ampoule, was standardized against potassium hydrogen phthalate. All dilute solutions were prepared from double-distilled water with a conductance equal to 1.2±0.1μS.

Apparatus

The electromotive force was measured using a Metrohm model 781 pH ion-meter (resolution ±0.1 mV), using a combined glass-pH electrode (model 6.0258.000). All titrations were carried out in a 80 mL thermostated double-walled glass vessel. Spectrophotometric measurements were performed on a UV-Vis Shimadzu 2100 spectrophotometer with a Pentium 4 computer and using thermostated matched 10 mm quartz cells. The measurement cell was of the flow type. A peristaltic pump allowed circulation of the solution under study from the potentiometric cell to the spectrophotometric cell, so the absorbance and the emf of the solution could be measured simultaneously. To exclude carbon dioxide from the system, a stream of purified nitrogen was passed through a sodium hydroxide solution and then bubbled slowly through the reaction solution.

Measurements

All measurements were performed inthe ionic strength ranging from 0.1 to 1.5 moldm^{-3} sodium perchlorate, sodium nitrate, and sodium chloride. The protonation constants were evaluated from the measurement of absorbance versus emf by titration of 50 mL of the nucleoside [(1.0-3.0)×10^{-3} mol·dm^{-3}] with 0.1 moldm^{-3} sodium hydroxide solution both with the same ionic strength at 25 °C. Potentiometer calibration was performed by the Gran's method [16]in terms of hydrogen ion concentration, by titrating a strong acid (0.01 moldm^{-3} HCl) with a strong base (0.1 moldm^{-3} NaOH) in the same condition of ionic strength to be used in later experiments. Also, in a similar procedure, a 50 mL acidic solution of Tl(I) [(1.0-3.0)×10^{-3} moldm^{-3}] was titrated with an alkali solution (0.1 moldm^{-3} NaOH) of CMP [(2.0-4.0)×10^{-3} moldm^{-3}] both with the same ionic strength. The potential, E, was allowed to stabilize after each addition of the titrant and is defined as:

$$E_{\text{cell}} = k_1 + k\log[\text{H}^+] + k\log \gamma_{\text{H}}^+ \qquad (1)$$

where k_1 comprises $E^{\text{o}}_{\text{cell}}$ and the junction potential, and $k = 2.303RT/F$ in which R, T, and F have the usual meanings. The calculated Nernstian parameter, k, was very close to its theoretical value and always in the range of 59.1-59.2. As the ionic strength is kept constant in each run, so the activity coefficient of hydrogen ion, γ, is constant too, and so:

$$E_{\text{cell}} = E'_{\text{a}} + k\log[\text{H}^+] \qquad (2)$$

where E'_{a} (the specific constant of the potentiometric cell) is $k_1 + k\log \gamma_{\text{H}}^+$. The non-ideality of solutions is then included in E'_{a}.

RESULTS AND DISCUSSION

Protonation of CMP

The protonation constants of CMP has been determined spectrophotometrically based on the relation $A = f(\text{pC}_\text{H})$ [17]. The measured absorbance, A, (270 to 320 nm) in the interval of 0.5 nm and pC$_\text{H}$(-log[H$^+$]) from the spectrophotometric titration were conducted with the computer program Squad [18-19]. The data in the computer program were fitted to Eqs. 3-4 by minimizing the error square sum of the difference in the experimental absorbances and the calculated ones. The program allows calculation of the protonation constants with different stoichiometries. The number of experimental points (absorbances versus pC$_\text{H}$) was more than 35 (maximum 50) for each titration run. During the experiments, the solutions were stable and the absorbance values did not change with time.

The results obtained using potentiometric-spectrophotometric titrations for the various acidity constants of the proton donors of CMP are listed in Table 1 together with some values reported in the literature [20-22]. In Fig. 1, the species mole fractions of CMP in different pC_H are shown in0.1 mol·dm^{-3} $NaClO_4$. The nucleotide shown in scheme 1, may bind with two protons at the phosphate group and one at the pyrimidine moiety. It was proposed [22]that $H_3(CMP)^+$ releases its first proton from $P(O)(OH)_2$, the second one from H(N3) and the third one again from the phosphate group. A forth proton is released in the alkaline pH range from ribose group. The first deprotonation of the nucleotide from the $P(O)(OH)_2$ (p$K<$ 1) and the last one from the ribose groups (p$K>$ 12) [22]are not considered further in this work. The given acidity constants agree well, as far as available, with those reported in recent compilations, Table 1 [20-22]. The small differences are possibly due to the different experimental method and the different background electrolyte used. These steps are expressed by the following equilibrium:

$$H(CMP)^{2-} + H^+ \xleftrightarrow{K_1} H_2(CMP)^- \qquad (3)$$

$$H_2(CMP)^- + H^+ \xleftrightarrow{K_2} H_3(CMP) \qquad (4)$$

Complexation of CMP by Tl(I)

One of the main obstacles in studying metal ion systems with nucleotide derivatives in solution are the known as the self-association of them. This means low concentration of the ligands must be employed in the experiments, a condition usually fulfilled with UV-spectroscopic studies. In similar studies Sigel et al [23] has demonstrated that in 1-5 mM solution about 95-97 % of the total nucleotide exists in the monomeric form. With the indicated problem in mind we decided to study the complexes of CMP with thallium (I) by evaluating precise stability data from spectrophotometric titrations.

The complex $M_xH_yL_z^{(x+y-nz)}$ that formed is characterized by its stoichiometry (x:y:z), where M and L represent the metal ion and the ligand, respectively. To determine the stability constant of the complexation, Eq.5 is defined by β_{xyz}:

$$xM^+ + yH^+ + zL^{n-} \xleftrightarrow{\beta_{xyz}} M_xH_yL_z^{(x+y-nz)} \quad (5)$$

Determination of the stability constant, β_{xyz}, based again on the relation $A = f(pC_H)$ was performed using the computer program Squad. Absorbance, A, and pC_H were measured as described before. Treatments of the spectrophotometric data (270-320 with an interval of 0.5 nm) obtained during the titrations as a function of the pC_H was conducted with the computer program. The program allows calculation of the stability constants with different stoichiometries models.

Considering Eq.5, different models including MHL, ML, and several protonated species were tested by the program. As expected, polynuclear complexes were systematically rejected by the computer program, as also were MH_2L_2, MHL_2, and ML_2, (the charges were omitted for simplicity). A value for MH_2L species was also calculated by the program, but the species were not considered further, because the estimated error in its formation constant was unacceptable, and its inclusion does not improve the goodness of the fit. The models finally chosen, formed by MHL and ML resulted in a satisfactory of numerical and graphical fitting. The calculated average values of the stability constants for different experiments are listed in Table 2. In Fig. 2 the equilibrium distribution of various species in Tl^++CMP system is shown as a function of pC_H in 0.1 mol·dm^{-3} $NaClO_4$. The calculations are based on the stability constant values given in Table 2. The curves clearly demonstrate that an increase of the pC$_H$ is accompanied by an increase in the formation of deprotonated complex species and the stability of the species quite depends on pC$_H$. The most stable complex species at pC$_H$= 3.1 and 7.9 are $TlHL^-$ and TlL^{2-}, respectively. However, at higher ionic strength, the complex formation shifted to lower pC$_H$ value which is possibly due to the higher stability constant of the species formed at the condition.

Table 1. Average values of the protonation constants of CMP at 25 °C and different ionic strengths of various supporting electrolytes, *I*.Some values reported in the literature are also reported for comparison[a]

I mol·dm^{-3}	log K_2 $NaClO_4$	log K_1 $NaClO_4$	log K_2 $NaNO_3$	log K_1 $NaNO_3$	log K_2 NaCl	log K_1 NaCl	Ref.
0.1	4.30	6.35	4.29	6.35	4.29	6.34	This work
0.3	3.89	5.97	3.79	5.90	3.65	5.86	″
0.5	3.84	5.96	3.64	5.78	3.34	5.54	″
0.7	3.89	6.01	3.64	5.71	3.17	5.36	″
1.0	4.07	6.29	3.70	5.75	2.99	5.17	″
1.5	4.47	6.71	3.91	6.01	2.88	5.07	″
0.1	4.24	5.97					20
0.1	4.35	6.35					21
0.1	4.33	6.19					22

[a] Uncertainties (average between three independent measurements) of the values are 0.06 or lower.

Table 2. Average values of log β_{MHL} and log β_{ML} for the system CMP+Tl(I) at 25 °C and different ionic strengths of $NaClO_4$[a]

I mol·dm^{-3}	log β_{MHL} $NaClO_4$	log β_{ML} $NaClO_4$	log β_{MHL} $NaNO_3$	log β_{ML} $NaNO_3$	log β_{MHL} NaCl	log β_{ML} NaCl
0.1	6.57	4.94	6.57	4.94	6.57	4.93
0.3	6.11	4.39	6.05	4.35	6.02	4.14
0.5	5.86	4.22	5.79	4.03	5.64	3.78
0.7	5.74	4.26	5.65	3.89	5.47	3.53
1.0	5.73	4.52	5.54	3.91	5.34	3.55
1.5	5.82	4.87	5.58	4.12	5.38	3.59
0.1 [b]	6.57	4.94				

[a] Uncertainties (average between three independent measurements) of the values are 0.06 or lower.

[b] The values are taken from ref. 24.

Dependence of protonation and stability constants on ionic strengthand medium

The thermodynamic protonation constant, *K*, for example for Eq. 3, is expressed as:

$$K_1 = \frac{a_{H_2(CMP)^-}}{a_{H(CMP)^{2-}}a_{H^+}} = \frac{\gamma_{H_2(CMP)^-}[H_2(CMP)^-]}{\gamma_{H(CMP)^{2-}}\gamma_{H^+}[H(CMP)^{2-}][H^+]} \qquad (6)$$

where a_i and γ_i are the activities and the activity coefficients of the species involved in protonation equilibrium, Eq. 3, respectively. At infinite dilution $I \longrightarrow 0$ and $\gamma \longrightarrow 1$, so:

$$K_1 = K_1^\circ \frac{\gamma_{H_2(CMP)^-}}{\gamma_{H(CMP)^{2-}}\gamma_{H^+}} \qquad (7)$$

where K^o is the protonation constant at infinite dilution. By taking logarithm from Eq. 7,

$$\log K_1 = \log K_1^\circ + \log \gamma_{H_2(CMP)^-} - \log \gamma_{H(CMP)^{2-}} - \log \gamma_{H^+} \qquad (8)$$

and inserting the activity coefficient of the species from the Debye-Huckel equation in Eq. 8, results:

$$\log K_1 = \log K_1^\circ - \Delta Z^2 A \frac{\sqrt{I_m}}{1+B\sqrt{I_m}} \qquad (9)$$

where *A* is the parameter of the Debye-Huckel equation (A = 0.509 $kg^{1/2}\cdot mol^{-1/2}$at 25 °C), $\Delta Z^2 = \Sigma(\text{charges})^2_{\text{products}} - \Sigma(\text{charges})^2_{\text{reactants}}$, I_m is the ionic strength in molal scale (the different values of I_m for various supporting electrolytes are listed in Table 3), and *B* is an empirical constant (see hereafter).

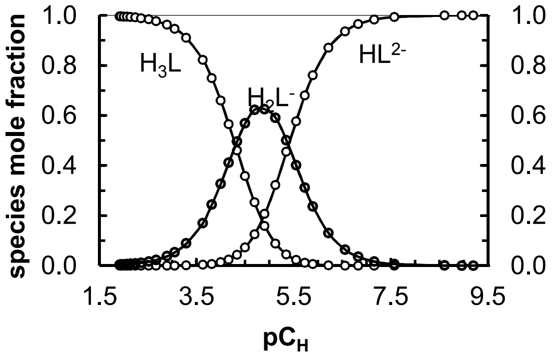


Fig. 1. Species distribution diagram of CMP at 25 °C and 0.1 mol·dm^{-3} NaClO$_4$.

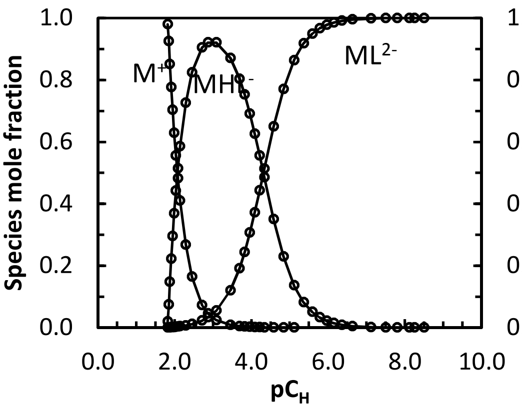


Fig. 2. Species distribution diagram of CMP+Tl$^+$ system at 25 °C and 0.1 moldm^{-3} NaClO$_4$.

Table 3. The different ionic strengths in molarity in terms of molality

I	*I* (mol·kg^{-1})		
(mol·dm^{-3})	NaClO$_4$	NaNO$_3$	NaCl
0.1	0.101	0.101	0.100
0.3	0.305	0.303	0.302
0.5	0.513	0.509	0.506
0.7	0.725	0.717	0.711
1.0	1.051	1.034	1.021
1.5	1.617	1.577	1.548

In the Debye-Huckel equation the long-range electrostatic interactions are taken into account, which dominates in dilute solution. However, in more concentrated electrolyte solution, short-range interactions have to be taken into consideration too. One possible way which first suggested by Bronsted and extended later by Guggenheim and Scatchard [25], is basically addition of a linear term, *C*, to the Debye-Huckel equation. This approach has been used successfully to describe the concentration dependence of formation constant and determination of formation constant at infinite dilution [26]. So, by rewriting Eq.9 and inserting the term, results:

$$\log K_1 = \log K_1^{\circ} - \Delta Z^2 A \frac{\sqrt{I_m}}{1+B\sqrt{I_m}} + \Delta C I_m \qquad (10)$$

where ΔC is the formation parameter to characterize the dependence on ionic strength and is$\Sigma C_{\text{products}} - \Sigma C_{\text{reactants}}$. The parameter ΔC, B, and log K° were then calculated by the fitting method using Eq. 11, and their values are given in Table 4 for all the protonation and stability constants in the different supporting electrolytes. The value of B in different conditions was very close to 1.5 which is consistent with the general Specific Ion Interaction Theory (SIT) [27]. Therefore, B is set equal to 1.5 in all the calculations (a small error in fixing B is absorbed in the term ΔC) [28].

$$S = \Sigma(\log K_{\text{exp}} - \log K_{\text{cal}})^2 \qquad (11)$$

The dependence of log K or β on ionic strength, Figs. 3 and 4, show a regular trend and are in agreement with other protonation constants of biological ligands and their complexation equilibria with some metal ions [13, 28]. Our previous results on ionic strength dependence of complex formation constants and this work reveal that log Kor βvalues are nearly always at their minimum at an ionic strength range 0.3-0.7 moldm^{-3}, which is possibly a characteristic of log $K = f(I)$.

The obtained empirical parameter, ΔC, using different supporting electrolytes to describe the dependence of protonation constants of CMP and its complexes with thallium (I) have different values and are in the order of $\Delta C_{\text{NaClO4}} > \Delta C_{\text{NaNO3}} > \Delta C_{\text{NaCl}}$, Table 3. The results of Tables 1 and2 suggesting that the Tl(I)-CMP system and the different species of the ligand are possibly more stable in sodium perchlorate than in the other supporting electrolytes. Figures 3 and 4, show good convergences of log K and log β to nearly a single value at lower ionic strength in all media.

The different supporting electrolytes used to keep constant the ionic strength may influence the protonation and the stability constant values in different ways. Indeed, the variation of the nature and the concentration of such electrolytes change the activity coefficient values and hence the formation constants. The effects of the ionic strength and the ionic medium on the formation constant values can be classified into two types: (a) the effects of changes on the activity coefficients, (b) specific interactions.

Table 4. Parameters for the dependence of ionic strength on protonation and stability constants at 25 °Cand in different media[a]

Species	ΔC			log K°		
	$NaClO_4$	$NaNO_3$	NaCl	$NaClO_4$	$NaNO_3$	NaCl
log K_2	3.58×10^{-1}	2.12×10^{-3}	-6.89×10^{-1}	4.17	4.18	4.23
log K_1	6.26×10^{-1}	1.34×10^{-1}	-5.05×10^{-1}	6.47	6.53	6.62
log β_{MHL}	-4.11×10^{-1}	-5.70×10^{-1}	-7.05×10^{-1}	6.27	6.27	6.24
log β_{ML}	3.82×10^{-1}	-1.63×10^{-1}	-4.62×10^{-1}	4.96	5.03	4.96

[a] Uncertainties (average between three independent measurements) of log K° are 0.06 or lower.

The formation constant values obtained in this work in all media have been adjusted to have the same ionic strength range, so the specific interactions should apparently be responsible for the observed differences in the studied systems, Tables 1 and 2.

The ionic strength dependence may be interpreted of the changes in the activity coefficients are related to the charges on the ionic species participating in the equilibrium. For example, in complexation of MHL^- neither charge compensation nor charge accumulation occur in the process. Indeed, there is a charge balance between the two sides of the reaction. This suggests the stability constant of MHL^- species in different supporting electrolytes should not differ significantly, which is consistent with the obtained results, Fig. 4. However, in processes with charge compensation or charge accumulation usually there is a considerable difference in formation constant in the different supporting electrolytes especially when the anion of the supporting electrolyte has a smaller size. This discussion is in agreement with the results obtained in this work. From among of very seldom work on this subject, complexation of copper (II)-glycine system (a charge compensation process) was studied in different ionic strengths and media (including $NaClO_4$, KNO_3, and KCl) [17].In the report, the determined formation constant of complexation has a larger value in $NaClO_4$ and a smaller one in KCl, as expected. This difference indicates the occurrence of a specific interaction in the given system; the authors concluded the formation of chloro-complexes. In another report, the protonation constants of sulphate ion were studied in the presence of various electrolytes and the same result was concluded. On the basis of the work, a weak but not insignificant complex formation takes place between the alkali metal ions and the sulphate ion.

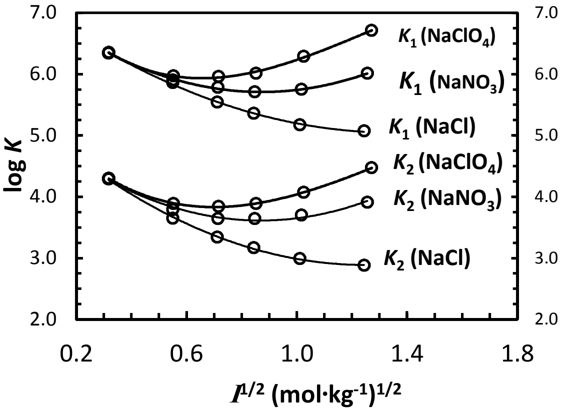


Fig. 3. Plots of log K_2 and log K_1 versus the square root of ionic strength at 25 °C and the different supporting electrolytes.

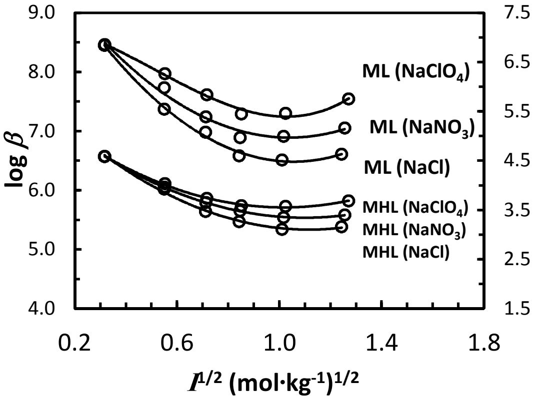


Fig. 4. Plots of log β_{MHL} and log β_{ML} versus the square root of ionic strength at 25 °C and the different supporting electrolytes.

CONCLUSIONS

The acid-base properties of cytidine 5′-monophosphate (CMP) and its complexation with thallium(I) ion are well described in the pH range 1.5 to 10.5, different ionic strengths (0.1-1.5 mol dm^{-3}), various ionic media ($NaClO_4$, $NaNO_3$, and NaCl), and 25 °C using potentiometric - spectrophotometric technique. The bonding sites of the ligand were determined and two mononuclear 1:1 species were specified. The general trend for the protonation constants of CMP and its complexes with thallium (I) ion are in the order of $NaClO_4$> $NaNO_3$> NaCl in different ionic media. The dependence of formation constants on ionic strength are described using a Debye-Huckel type equation and interpreted for the various supporting electrolytes.

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