

Interactions of Thymine and Uracil with Copper, Cobalt and Silver Ferrocyanides and the Implications in Chemical Evolution

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Authors' contributions

This work was carried out in collaboration between both authors. Author DD done the research project work, performed statistical analysis and wrote the first draft of the manuscript. Author BBT as supervisor of the research project managed the analysis of the study. Both authors read and approved the final manuscript.

Article Information

DOI: 10.9734/CJAST/2020/v39i830590

Editor(s):

(1) Dr. Aleksey Aleksandrovich Hlopitskiy, Ukrainian State University of Chemical Technology, Ukraine.

Reviewers:

(1) Hengguang Li, Fayetteville State University, USA.

(2) Randa Mohammed Osman, National Research Centre, Egypt.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/56014>

Original Research Article

Received 14 February 2020

Accepted 22 April 2020

Published 02 May 2020

ABSTRACT

Effects on pH based adsorption of nucleic acid bases (thymine and uracil) at two different concentrations 1×10^{-4} M and 1×10^{-5} M on copper, cobalt and silver ferrocyanides were studied over a pH range (1.0 – 10.0) at temperature $30 \pm 1^\circ\text{C}$. The progress of adsorption was followed spectrophotometrically by measuring the UV absorbance of the nucleic acid base solutions at their corresponding λ_{max} . Maximum adsorptions were found at neutral pH for both thymine and uracil. Effects of concentrations on adsorption of thymine and uracil on copper, cobalt and silver ferrocyanides were studied in a concentration range 10^{-4} – 10^{-5} M at neutral pH 7.0 ± 0.1 and at temperature $30 \pm 1^\circ\text{C}$. The interaction followed the Langmuir type of adsorption in general in the concentration range of 10^{-4} to 10^{-5} M of thymine and uracil solution. The uptake of nucleic bases on metal ferrocyanides followed the order of $\text{CuFc} > \text{AgFc} > \text{CoFc}$ for the adsorption of thymine and $\text{CuFc} > \text{CoFc} > \text{AgFc}$ for the adsorption of uracil. Effects of the presence of salts on the adsorption of thymine and uracil on metal ferrocyanides also had been studied. The insoluble metal ferrocyanides' interaction with biomolecules must have either formed metal complexes or could have enhanced the formation of biopolymers in fluctuating environment.

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Keywords: Interaction; thymine; uracil; nucleic bases; metal ferrocyanides; chemical evolution; origins of life.

1. INTRODUCTION

Due to easy of formation of cyanide under prebiotic conditions, cyanide ion might have formed stable complexes with transition metal ions on primitive earth. It is also thought that during the course of chemical evolution, cyanide could have also formed some insoluble double metal ferrocyanides of general formula $M_2 [Fe(CN)_6] \cdot x H_2O$ where M are Cu, Co, Mo, Ag, etc. It is well established that metal ferrocyanides act as adsorbents [1] and photosensitizers [2].

All organisms on Earth today use the same four bases in the same genetic code and the same twenty amino acids (out of the hundreds possible). Furthermore they all use the same basic mechanism of DNA-protein conversion. Even more surprising is that the genes specifying certain functions in vastly different creatures are very similar in their sequence of bases; homologous [3].

This research is specifically concerned with one of the essential life molecules, which is nucleic acid base that forms links along the double helix structure of deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). These nucleic acid bases may have aligned themselves over millenniums under varying chemical conditions and it is highly probable that the correct conditions and alignment may have occurred at some point in time resulting in the formation of a meaningful chemical structure that eventually evolved to be the first life form on Earth. This alignment was enhanced by the process of adsorption that allows an adsorbent to adsorb these nucleic acid bases onto its surface to facilitate chemical bonding.

The adsorbent that aided this proposed condensation of nucleic acid bases has to be a prebiotic molecule. Due to their solid surfaces, various clay minerals, silica and carbon have been proposed to play important roles in concentrating the biomolecules from dilute prebiotic soup in the primeval seas during the course of chemical evolution. Interaction with a wide variety of organic molecules including amino acids, peptides, nucleic acids and sugars with clay and clay minerals have been studied suggesting their possible role in chemical evolution [4].

The adsorption of pyrimidine on the loughlinitic Lewis acid sites through the pyrimidine lone pairs has been discussed [5]. The electrochemical behaviour of purine bases and their derivatives is studied on electrodes modified with carbon nanotubes. The strongest adsorption and oxidations are observed at +0.8 V and +1.0 V for guanine and adenine, respectively, [6]. The adsorption of purine on Ge (100) has been investigated using scanning tunnelling microscopy (STM) supported by *ab initio* theoretical calculations [7].

The adsorption behaviour of nucleosides (adenosine, guanosine and thymidine) on mesoporous silica, porous carbons and carbon nanocage were studied [8]. The plane wave density functional theory methods have been used to explore the adsorption modes and configurations of uracil molecules on a gold surface to gain insight into the rational design of surface functionalization [9]. The adsorption sites of adenine, adenosine, AMP, ADP, ATP, Poly A, uracil, uridine, UMP, UDP, UTP and Poly U on sodium montmorillonite are investigated [10].

The interaction of adenine and thymine with and adsorption on zeolites were studied by using FT-IR, EPR spectroscopy, X-RD and SEM Studies. It is observed from X-RD that thymine adsorption increased the decomposition of zeolites while adenine prevented it. Zeolite adsorbed some amount of adenine and thymine protected from hydrolysis and UR radiation could be available for molecular evolution [11]. Computational study performed using the density functional theory shows that hydrated and non-hydrated tetrahedral and octahedral kaolinite mineral surfaces in the presence of a cation adsorb the nucleic acid bases thymine and uracil well [12].

Adsorption of adenine was studied in the presence of montmorillonite clay with or without cations Ca^{2+} , Cu^{2+} and Mg^{2+} . Results of present study showed that adsorption trend largely depend on the nature of adsorbate and the adsorbent [13]. Interaction of mono-, oligo- and polynucleotides and their components on rutile (TiO_2) has been important for the origin of life. TiO_2 is a mineral common in many terrestrial crustal rocks [14]. Several prebiotic experiments including (a) primary chondrite minerals (Olivine,

Pyroxene etc.) and clay modified with metals (Cu, Fe, Ni, Mo, Zn, etc.) (b) using mineral with more organophilic characteristics (c) using sea water of different conc. of ions (i.e. Na^+ , Cu^{2+} , Mg^{2+} , SO_4^{2-} and Cl^-) (d) determine possible products of decomposition due to interactions of amino acids and nucleic acid bases with minerals are reported to understand important issues related to origin of life on Earth [15]. The adsorption of purines, pyrimidines and nucleosides from aqueous solution to clay minerals is affected by suspension pH. With montmorillonite adsorption is also influenced by the nature of the exchangeable cations [16].

Adsorptive interaction of nucleotides on the rutile (110) surface is investigated [17]. The possible role of montmorillonite clays in the prebiotic formation of RNA is discussed and it is also concluded from this study that ligation to the Cu^{2+} is a major force in the binding of nucleotides to Cu^{2+} -montmorillonite and are not readily washed from the clay [18]. Adsorption of adenine on the surface of graphite crystals have been studied at different temperature. Results suggest that the effects of temperature and presence of inorganic solids must be included when assessing the prebiotic availability of adenine [19]. Catalytic guanine oxidation using $\text{Ru}(\text{bpy})_3^{2+}$ as mediator has been investigated electrochemically in viscous solutions containing high concentration of polyethylene glycol. DNA adsorption increase with increasing the viscosity of its solution and produces pre peaks in cyclic voltagrams [20]. Difference spectra have been observed in both adsorption and circular dichroism upon binding of various guanine nucleotides to ribonuclease F1 [21]. Very few reports are available on interactions of amino acids with metal ferrocyanides (MFcs) and no reports are available on interaction of nucleic acid bases with MFcs. An attempt was made to study interaction of nucleic acid bases with MFcs. In addition, the present work described the interactions of thymine (Thy) and uracil (Ura) with copper ferrocyanide (CuFc), Cobalt ferrocyanide (CoFc) and silver ferrocyanide (AgFc) as well as their implications in chemical evolution.

2. EXPERIMENTAL

2.1 Chemicals

Copper nitrate, cobalt nitrate, silver nitrate, potassium ferrocyanide, thymine and uracil were obtained from BDH Poole, England. All chemicals were of analytical grade and used

without further purification. Solutions were prepared in doubly distilled water.

2.2 Synthesis of Metal Ferrocyanides

Copper and cobalt ferrocyanides were prepared by adding metal salts (500 mL, 0.1 M) and potassium ferrocyanide (167 mL, 0.1 M) with constant stirring [22]. A slight excess of the metal salt was added to the mixture to enhance coagulation of the precipitate. The reaction mixture was then heated at 60°C in a water bath for 3 hours and was kept as such for 24 hours at room temperature. The precipitate was filtered using vacuum filtration and washed several times with distilled water. The precipitate was then kept in an oven pre-set at $60\text{--}65^\circ\text{C}$ for 2 hours until dried. The dried product was then grounded using a mortar and pestle and was sieved using a $125\ \mu\text{m}$ mesh size sieve. The same procedure was used to produce silver ferrocyanide except that silver nitrate salt was used instead and the system was kept protected from light by being wrapped with aluminum foil and were performed in dark chamber.

2.3 Characteristics of Metal Ferrocyanides

Copper ferrocyanide is a rust brown, grainy insoluble solid. Cobalt ferrocyanide is grey blackish in colour and is an amorphous insoluble solid that possesses an octahedral structure with face centred cubic lattice. Silver ferrocyanide is a blue, powdery and insoluble solid.

They were characterized on the basis of elemental and spectral studies. The percentage composition of metals was determined by Varian Techtron atomic absorption spectrophotometer [23]. Carbon, hydrogen, nitrogen analysis was performed on CEST – 118, CHN analyser. The elemental analysis percentage values metal ferrocyanides are given in Table 1.

Infrared spectra of compounds were recorded in potassium bromide disc on Beckmann IR-20 spectrometer. All three metal ferrocyanides show a broad peak at $3600 - 3625\ \text{cm}^{-1}$ is characteristics of water molecules and OH group. Also a peak around $1600 - 1635\ \text{cm}^{-1}$ due to H-O-H bending. Two sharp bands one at $2010 - 2080\ \text{cm}^{-1}$ and other at $580 - 600\ \text{cm}^{-1}$ in all three metal ferrocyanides are characteristics of -CN and Fe-C stretching frequencies [24]. Another sharp band at around $460 - 490\ \text{cm}^{-1}$ probable shows the presence of metal (Cu, Co, Ag) –

nitrogen band thus indicating a certain degree of polymerization in the product [25,26]. Infrared spectral data of copper, cobalt and silver ferrocyanides are given in Table 2.

2.4 Adsorption Studies

2.4.1 Effects of pH on adsorption of nucleic acid bases on metal ferrocyanides

Buffer solutions for pH 1.0-10.0 were prepared using the reagents and their respective concentrations as shown in Table 3.

The PH's were verified with a Fisher Scientific pH meter. Effects of pH on adsorption of thymine and uracil on metal ferrocyanides were studied at two different concentrations 1×10^{-4} M and 1×10^{-5} M over pH range 1.0 – 10.0 and at temperature $30 \pm 1^\circ\text{C}$. Two different concentrations 10^{-4} M and 10^{-5} M of thymine and uracil solutions were prepared in the buffer

solutions. 10 ml of buffered thymine and uracil were added to their respective labelled cuvettes and the initial absorbance of the solutions was measure by a Hach DR 5000 UV Spectrometer at 264.5 nm and 258.0 nm for thymine and uracil respectively. 100 mg of each of the three metal ferrocyanides was then added to each centrifuge tube and the mixture was placed on a Stuart Scientific Flask Shaker at speed 10 at room temperature for 8 hours with manual shaking at a regular 1 hour interval. The mixtures were then centrifuged using an Eppendorf Centrifuge and the supernatant was decanted and collected. The final absorbance of the supernatant was measured using the UV spectrometer at their respective λ_{max} values. The percentages uptake of the nucleic acid bases by metal ferrocyanides were calculated for each of the pH. It was found that the type of buffers used do not adsorb on the surface of metal ferrocyanides. This was confirmed by conductivity measurements.

Table 1. Elemental analysis of copper, cobalt and silver ferrocyanides

Metal ferrocyanides	Percentage (%) found				
	Metal	Iron	Carbon	Hydrogen	Nitrogen
CuFc ^a	28.30	12.40	16.03	2.56	18.32
CoFc ^b	26.60	13.10	15.50	2.71	18.10
AgFc ^c	40.22	8.75	11.47	2.75	13.77

^a CuFc = Copper ferrocyanide, ^b CoFc = Cobalt ferrocyanide, ^c AgFc = Silver ferrocyanide

Table 2. Infrared spectral data of copper, cobalt and silver ferrocyanides

Metal ferrocyanides	Absorption frequency (cm ⁻¹)				
	H ₂ O molecule OH group	HOH Bending	C \equiv N Stretching	Fe – C	Metal – N ^a
CuFc	3700	1600	2080	580	490
CoFc	3510	1635	2070	595	460
AgFc	3800	1600	2010	600	490

^aMetal – nitrogen band shows degree

Table 3. Reagents and their respective concentrations used in the preparation of buffer solutions pH 1.0 to 10.0

pH	Reagents and concentrations (M)	
1.0	0.2 KCl	0.2 HCl
2.0	0.2 KCl	0.2 HCl
3.0	0.1 HOAc	0.1 NaOAc
4.0	0.1 HOAc	0.1 NaOAc
5.0	0.1 HOAc	0.1 NaOAc
6.0	0.1 HOAc	0.1 NaOAc
7.0	0.1 KH ₂ PO ₄	0.1 NaOH
8.0	0.1 Na ₂ B ₄ O ₇ · 10 H ₂ O	0.1 HCl
9.0	0.025 Na ₂ B ₄ O ₇ · 10 H ₂ O	0.1 HCl
10.0	0.025 Na ₂ B ₄ O ₇ · 10 H ₂ O	0.1 NaOH

2.4.2 Effect of concentration on the adsorption of thymine and uracil on copper, cobalt and silver ferrocyanides

The adsorption of thymine and uracil on metal ferrocyanides as a function of concentration range 10^{-4} - 10^{-5} M was studied at pH 7.0 ± 0.01 and at temperature 30 ± 1 °C. A buffer of pH 7.0 was made using potassium dihydrogen phosphate and sodium hydroxide. Stock solutions of concentration 1×10^{-4} M of thymine and uracil were prepared. These two stock solutions were further diluted using the buffer solution to give the range of concentration from 10^{-4} M to 10^{-5} M. A 10 ml of buffered thymine and uracil solutions at each respective concentration were added to a series of test tubes and the initial absorbance was measured using the Hach DR 5000 UV spectrophotometer. A 100 mg of each of the three metal ferrocyanides was then added to each centrifuge tube and the mixture was placed on a shaker at speed 10 at room temperature for 8 hours with manual shaking at a regular 1 hour interval. The mixtures were then centrifuged and the supernatant was decanted and collected. The final absorbance of the supernatant was measured by UV spectrometer at their respective, λ_{\max} values. The amount of thymine and uracil adsorbed on the surfaces of three metal ferrocyanides was calculated for each of the concentration.

2.4.3 Effect of salts on the adsorption of thymine and uracil on copper, cobalt and silver ferrocyanides

The effect of copper nitrate, cobalt nitrate and silver nitrate on the adsorption of thymine and uracil nucleic bases on metal ferrocyanides was studied by carrying out separate experiments at varying concentrations in the presence of 1.5×10^{-3} M of each salt used to prepare the three metal ferrocyanides. This experiment was conducted at pH 7.0 ± 0.01 and room temperature. A buffer of pH 7.0 was made using potassium dihydrogen phosphate and sodium hydroxide. A known calculated mass of each of the three metal salts: copper nitrate, cobalt nitrate, and silver nitrate, was measured. They were all dissolved in separate quantities of the pH 7.0 buffer to acquire a salt concentration of 1.5×10^{-3} M in each case. Stock concentrations of 10^{-4} M of thymine and uracil solutions were prepared using the salt-buffer solution. These two stock solutions were further diluted using the buffer solution to give a range of concentration of thymine and uracil from 1×10^{-4} M to 1×10^{-5} M.

A 10 ml of buffered thymine and uracil salt solutions at each respective concentration were added to a series of test tubes and the initial absorbance was measured by UV spectrometer. A 100 mg of each of the three metal ferrocyanides was then added to each centrifuge tube containing its own respective salts solutions and the mixture was placed on a shaker at speed 10 at room temperature for 8 hours with manual shaking at a regular 1 hour interval. The mixtures were then centrifuged at 1/2000 rpm and the supernatant was decanted and collected. The final absorbance of the supernatant was measured at their respective, λ_{\max} values. The amount of the thymine and uracil adsorbed on metal ferrocyanides was calculated for each of the concentration.

At salt concentration 1.5×10^{-3} mol / L and pH 7.0 ± 0.01 , the copper, cobalt and silver hydroxides do not get adsorbed on the surface of metal ferrocyanides. This was verified by conductivity measurements of salt solution with and without metal ferrocyanides [27].

3. RESULTS AND DISCUSSION

3.1 Effect of pH on the Adsorption of Thymine and Uracil on Metal Ferrocyanides

The percentage uptake of thymine and uracil was studied over the pH range of 1.0 – 10.0. Two different concentrations of the nucleic acid bases were used in this part of the investigation 10^{-4} M and 10^{-5} M. The effects of pH on the adsorption of thymine and uracil on copper, cobalt and silver ferrocyanides are shown on Figs. 1 and 2. The percentage uptake was calculated using the following formula.

$$\text{Percentage Uptake} = \frac{\text{Difference in absorbance before and after adsorption}}{\text{Absorbance before adsorption}} \times 100$$

For both concentrations of thymine and uracil used, the maximum uptake occurred at neutral pH. According to Fig. 1 that shows the percentage uptake of thymine and uracil at an initial concentration of 1×10^{-5} M, the most effective metal ferrocyanide in adsorbing thymine and uracil was found to be Cobalt ferrocyanide (66.0% for Thymine and 65.0% for Uracil). Copper ferrocyanide also was very effective in adsorbing thymine and uracil at this concentration. The least effective metal ferrocyanide was found to be silver ferrocyanide.

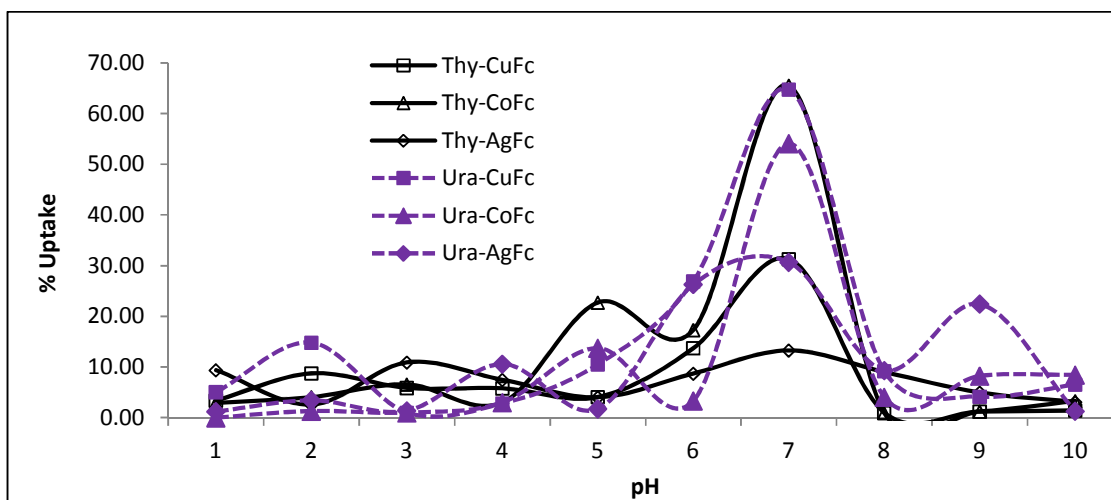


Fig. 1. Effect of pH on the adsorption of thymine and uracil (concentration = 1×10^{-5} M) on metal ferrocyanides

(Temperature = $30 \pm 1^\circ \text{C}$; time = 8 hours; mass of MFC = 100 mg; particle size = $125 \mu\text{m}$; thymine $\lambda_{\text{max}} = 264.5 \text{ nm}$; uracil $\lambda_{\text{max}} = 258.0 \text{ nm}$)

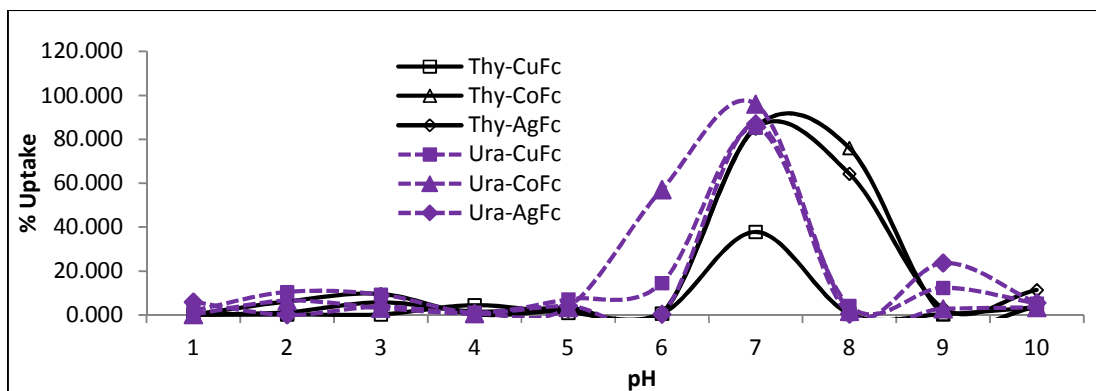


Fig. 2. Effect of pH on the adsorption of thymine and uracil (concentration = 1×10^{-4} M) on metal ferrocyanides

(Temperature = $30 \pm 1^\circ \text{C}$; Time = 8 hours; Mass of MFC = 100 mg; Particle Size = $125 \mu\text{m}$; Thymine $\lambda_{\text{max}} = 264.5 \text{ nm}$; Uracil $\lambda_{\text{max}} = 258.0 \text{ nm}$)

For a higher initial concentration of thymine and uracil (1×10^{-4} M as shown in Fig. 2), the overall percentage uptake was found to have been elevated. The most effective metal ferrocyanide in adsorbing thymine and uracil was found to be cobalt ferrocyanide (76.0% and 96.0%, respectively). The percentage uptake values of thymine and uracil at concentrations 10^{-4} M and 10^{-5} M on copper, cobalt and silver ferrocyanides are given in Table 4.

Generally, it can be seen that as the concentration of the nucleic acid bases increases, the percentage uptake also increases. A high concentration means that more of the

nucleic bases' molecules are available to bind to active sites on the adsorbent. Sufficient adsorbent molecules are available to occupy the active sites unlike in the situation where a deficient of such molecules are used leading to a low uptake. The percentage uptake of uracil is overall higher compared to that of thymine. This is solely due to the chemical structure of the two molecules.

Due to the absence of the methyl group in uracil, the double bond becomes more electron-deficient since methyl groups are strong electron donors. As a result, it is with much ease that a bond can result between uracil and a metal

Table 4. Percentage adsorption of thymine and uracil at different initial concentrations on the copper, cobalt and silver metal ferrocyanides

% Adsorption											
CuFc				CoFc				AgFc			
1 x 10 ⁻⁴ M		1 x 10 ⁻⁵ M		1 x 10 ⁻⁴ M		1 x 10 ⁻⁵ M		1 x 10 ⁻⁴ M		1 x 10 ⁻⁵ M	
Thy	Ura	Thy	Ura	Thy	Ura	Thy	Ura	Thy	Ura	Thy	Ura
0.13	1.98	3.39	5.06	0.26	0.24	2.91	0.00	0.24	5.96	9.38	1.23
0.26	10.48	8.75	14.80	1.29	6.51	4.05	1.29	6.15	0.13	2.56	3.45
0.33	9.31	5.88	1.00	5.82	3.13	6.56	0.98	9.61	3.91	10.91	1.39
4.47	1.13	5.80	2.82	1.64	0.74	2.99	2.99	0.33	0.74	7.46	10.61
1.06	7.17	4.08	10.53	3.32	3.53	22.73	13.73	1.98	4.22	4.00	1.75
0.67	14.62	13.73	26.92	0.93	57.12	17.31	3.33	0.50	0.41	8.70	26.32
37.87	85.35	31.31	64.77	85.53	96.04	65.56	54.12	84.91	87.07	13.28	30.68
0.58	4.15	0.99	9.21	76.04	1.74	0.93	4.05	64.32	0.50	9.01	9.33
0.41	12.37	1.22	4.17	0.41	2.82	1.22	8.22	3.18	23.73	4.97	22.45
3.58	5.30	1.43	6.54	3.38	3.48	3.28	8.43	11.39	5.55	3.08	1.30

(Temperature 30 ± 1°C; Mass of MFC = 100 mg; Particle Size = 125 µm; Thymine λ_{max} = 264.5 nm; Uracil λ_{max} = 258.0 nm)

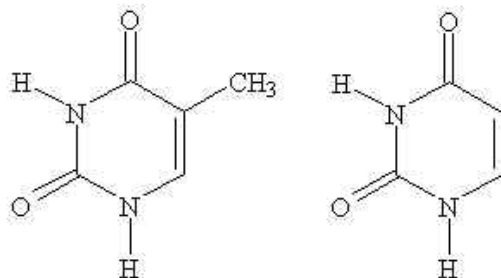


Image 1: Thymine

Image 2: Uracil

ferrocyanide than between the latter and thymine. As a result, the metal ferrocyanides are more prone to bond to the electron-deficient uracil resulting in a higher percentage uptake than that of thymine.

The adsorption of thymine and uracil occurred at neutral pH for all the systems investigated. The characteristic tautomeric nature of bases provides some insight into the pH effect [28-32]. Under acidic conditions, bases occur as the cations and as neutrality is approached, they tend to shift to the more stable tautomeric forms. When the pH is greater than 7.0, this gives an indication that adsorption is taking place in the form of anions. In acidic conditions, the carbonyl form dominates; at neutral pH, the more stable tautomeric form results and beyond pH 7.0, the tautomeric form changes to give the phenolic structures. Adsorption of bases on metal ferrocyanides could be due to base interactions with replaceable divalent metal ions such as Cu (II), and Co (II) present outside the coordination sphere of the metal ferrocyanides [33]. Considerable decrease in adsorption of bases on the metal ferrocyanide for both of the concentrations investigated (10^{-4} M and 10^{-5} M) may be because at higher pH, the coordination of available OH^- ions with divalent cations (Cu^{2+} , Co^{2+}) and monovalent Ag^+ becomes competitive with that of the thymine and uracil molecules. Thymine and uracil are adsorbed best onto metal ferrocyanides at neutral pH.

3.2 Effect of Concentration on the Adsorption of Thymine and Uracil on Metal Ferrocyanides

This part of the experiment was carried out at pH 7 ± 0.01 since it was seen from the latter section that adsorption of thymine and uracil occurs best in a pH-neutral system. Room temperature ($30 \pm 1^\circ\text{C}$) was also employed

to carry out this part of the investigation. A series of standard solutions of concentration ranging from 10^{-5} M to 10^{-4} M were prepared using the two thymine and uracil separately and the system solvent (pH 7.0 ± 0.01 buffer).

It is clear in Fig. 3 that at lower concentrations of thymine and uracil, the adsorption is rapid but at greater concentrations the uptake becomes almost constant. This holds true for all the system investigated with a positively sloping line and a flat tail. This phenomenon is quite adhering to the adsorption theory. As the number of adsorbate (bases) molecules increases, more will be available to be bound to the adsorbent (metal ferrocyanide) molecules. The adsorbent usually have a fixed number of adsorption sites and when all of these sites are occupied by the adsorbate molecules, a saturation point is reached where even increasing the adsorbates concentration will lead to no further binding [34]. The latter statement holds true for a Langmuir adsorption process where monolayer coverage occurs and no other molecules can bind after all the sites are occupied. The values of maximum uptake of thymine and uracil on the different metal ferrocyanides are given in Table 5.

The orders of maximum uptake of thymine and uracil observed on metal ferrocyanides:

Thymine: Cobalt ferrocyanide < silver ferrocyanide < Copper ferrocyanide

Uracil: Silver ferrocyanide < Cobalt ferrocyanide < Copper ferrocyanide

Langmuir plot ($1/Q_{\text{eq}}$ versus $1/C_{\text{eq}}$) for the adsorption of thymine and uracil on copper, cobalt and silver ferrocyanides are shown on Fig. 4.

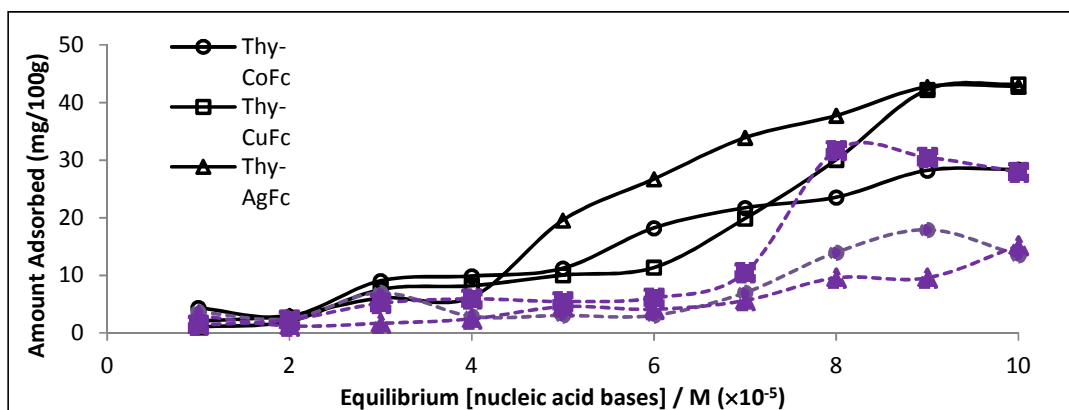


Fig. 3. Adsorption isotherms of thymine and uracil on metal ferrocyanides
 (Temperature = $30 \pm 1^\circ\text{C}$ time = 8 hours; pH = 7.0 ± 0.01 ; mass of MFC = 100 mg; particle size= 125 μm ;
 Thymine $\lambda_{\text{max}} = 264.5 \text{ nm}$; uracil $\lambda_{\text{max}} = 258.0 \text{ nm}$)

Table 5. Maximum uptake of thymine and uracil on metal ferrocyanides

Nucleic acid base	Metal ferrocyanide	Particle size (μm)	Maximum Uptake, $\times 10^{-7}$ [mol/g]
Thymine	CuFc	125	34.25
	CoFc	125	22.50
	AgFc	125	33.94
Uracil	CuFc	125	28.28
	CoFc	125	15.97
	AgFc	125	13.53

(Temperature = $30 \pm 1^\circ\text{C}$; pH 7.0 ± 0.01)

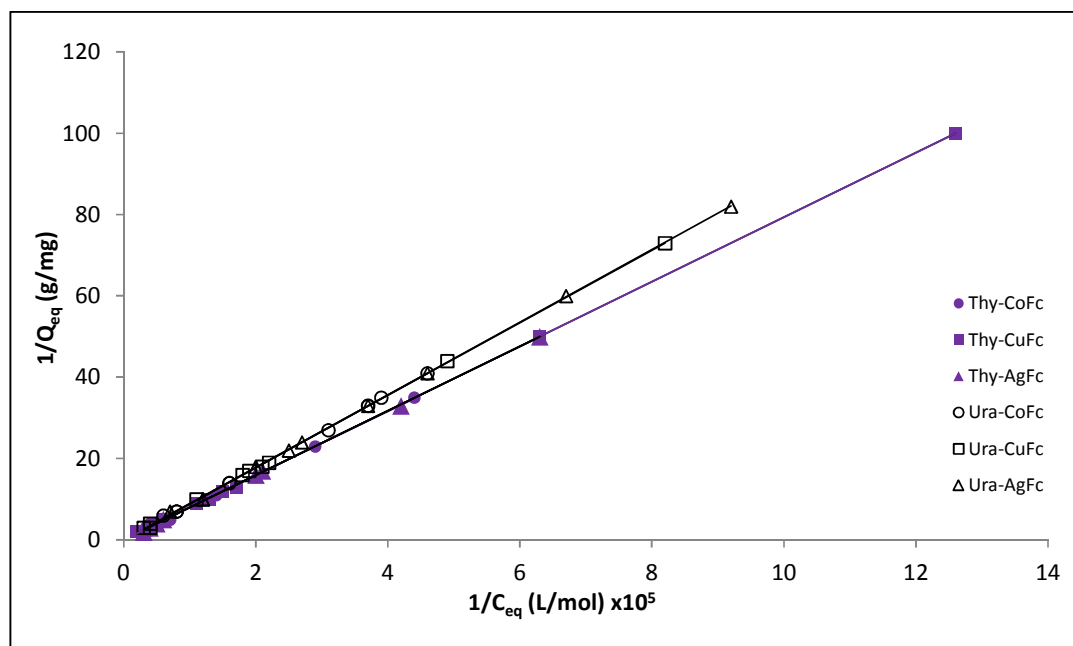


Fig. 4. Langmuir plots of thymine and uracil on metal ferrocyanides
 (Temperature = $30 \pm 1^\circ\text{C}$ time = 8 hours; pH = 7.0 ± 0.01 ; mass of MFC = 100 mg; particle size= 125 μm ;
 Thymine $\lambda_{\text{max}} = 264.5 \text{ nm}$; uracil $\lambda_{\text{max}} = 258.0 \text{ nm}$)

The linearized form of the Langmuir equation was considered to develop the linear plots. The adsorption isotherms for thymine and uracil have been analysed in terms of the Langmuir adsorption equation [35]:

$$\frac{1}{Q_{eq}} = \frac{1}{Q_0} + \frac{1}{Q_0 b} \cdot \frac{1}{C_{eq}}$$

where Q_{eq} is the amount of solute adsorbed per unit mass of adsorbent, C_{eq} the equilibrium concentration of solute in solution, Q_0 the limiting amount of adsorbate that can be taken up by unit mass of adsorbent, b the constant related to equilibrium constant or bonding energy or enthalpy (ΔH) of adsorption ($b \propto e^{-\Delta H/RT}$ the parameter b reflects the steepness of the approach to saturation; more precisely, the b value is the reciprocal of concentration at which half of the saturation of the adsorbent is attained). Actually "b" is a constant, which is function of adsorption energy. The appropriate Langmuir constants b and Q_0 were calculated from the slope and intercept of the Langmuir plots respectively. The values of Langmuir constants are given in Table 6.

3.3 Effect of Salt on the Adsorption of Thymine and Uracil on Metal Ferrocyanides

Effect of salts on the adsorption of thymine and uracil on Copper ferrocyanide, Cobalt ferrocyanide and silver ferrocyanide at

their equilibrium concentrations are shown in Fig. 5.

The values of maximum uptake of thymine and uracil are given in Table 7. The orders of maximum adsorption of nucleic acid bases on metal ferrocyanides in the presence of salts are as follows:

Thymine: Cobalt ferrocyanide < silver ferrocyanide < Copper ferrocyanide

Uracil: Silver ferrocyanide < Copper ferrocyanide < Cobalt ferrocyanide

In each experiment the values of maximum adsorption was found to be higher in the presence of salts in comparison to absence of salts.

This indicates that added metal ions (Cu^{2+} , Co^{2+} , and Ag^+) either first make complexes with the nucleic acid bases and then get adsorbed on the metal ferrocyanides surface or that the increase in ionic strength upon addition of the metal salt solution lowers the repulsive forces between the organic molecules and the metal ferrocyanide or that both of these mechanism are operative. Studies on salt effects have confirmed the assumption that at normal conditions adsorption is due to the formation of nucleic acid base-metal complexes [27]. This is also assumable since it is unlikely for the nucleic acid base (thymine and uracil) molecule to enter into the coordination

Table 6. Langmuir constants for the adsorption of thymine and uracil on metal ferrocyanides

Nucleic acid base	Metal ferrocyanide	Particle size (μm)	Langmuir constants	
			b (Lmol^{-1}) $\times 10^{-11}$	Q_0 (mg g^{-1}) $\times 10^{14}$
Thymine	CuFc	125	5.00	2.50
	CoFc	125	25.00	0.50
	AgFc	125	5.00	2.50
Uracil	CuFc	125	11.11	1.00
	CoFc	125	33.33	0.33
	AgFc	125	22.22	0.50

(Temperature = $30 \pm 1^\circ\text{C}$; pH 7.0 ± 0.01)

Table 7. Maximum uptake of thymine and uracil on metal ferrocyanides in the presence of salts

Nucleic acid base	Metal ferrocyanide	Particle size (μm)	Salts [1.5×10^{-3} M]	Maximum Uptake, $\times 10^{-7}$ [mol/g]
Thymine	CuFc	125	CuCl_2	35.52
	CoFc	125	$\text{Co}(\text{NO}_3)_2$	21.97
	AgFc	125	AgNO_3	34.81
Uracil	CuFc	125	CuCl_2	32.21
	CoFc	125	$\text{Co}(\text{NO}_3)_2$	55.76
	AgFc	125	AgNO_3	14.75

(Temperature = $30 \pm 1^\circ\text{C}$; pH 7.0 ± 0.01)

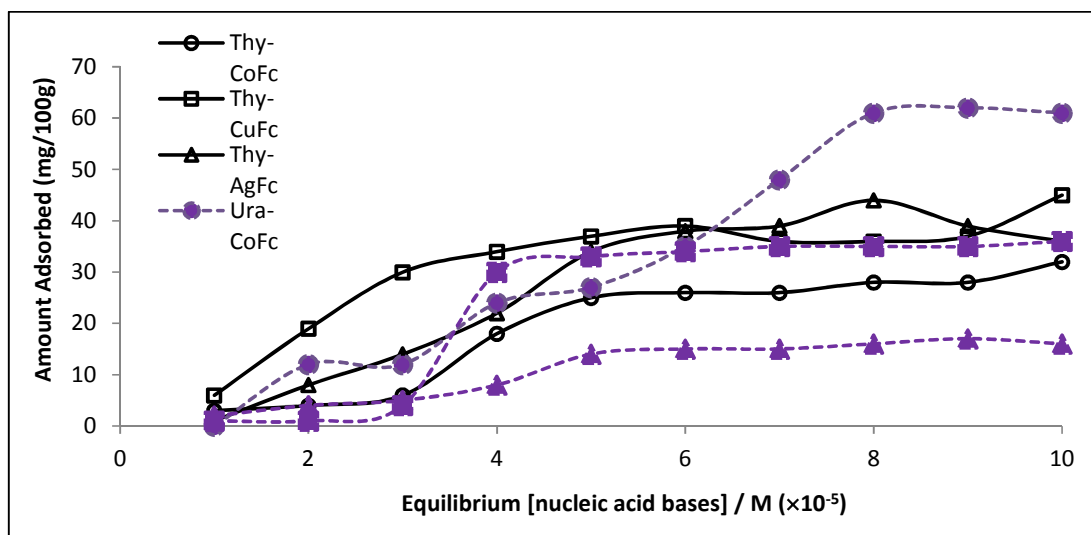


Fig. 5. Adsorption isotherms of thymine and uracil on metal ferrocyanides in the presence of salt

(Concentration of Salt = 1.5×10^{-3} M; temperature = $30 \pm 1^\circ\text{C}$ time = 8 hours; pH = 7.0 ± 0.01 ; mass of MFc = 100 mg; Particle size = 125 μm ; thymine $\lambda_{\text{max}} = 264.5$ nm; uracil $\lambda_{\text{max}} = 258.0$ nm)

sphere of metal ferrocyanides by replacing strong ligands like cyanide. As such, some form of complexation is very possible that ultimately increases the binding capacity of the adsorbate to the adsorbent.

Lahav and Chang proposed a model for a prebiotic environment in which concentration, condensation and chemical evolution of biomolecules could have taken place. In this model, however, high concentration of soluble salts, such as chlorides and sulphates, are taken into account, where as previously more or less salt-free system had been assumed. The proposed system emphasises the need to develop the theoretical background and experimental methods for the study of interactions among biomolecules in the presence of high salt concentrations and solid surfaces soluble salts, as well as interaction between the biomolecules and these surfaces [36-38].

4. CONCLUSION

The results of the present study reveal that insoluble metal ferrocyanides present at the bottom and on shores of primeval seas could have interacted with thymine and uracil in such a way as to concentrate them from the dilute prebiotic soup during the course of chemical evolution.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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