Surface Interaction of Adenine on Montmorillonite Clay In Presence And Absence of Divalent Cations In Relevance To Chemical Evolution

Kavita Gururani, Chandra Kala Pant, Hari Datt Pathak

Abstract: Bernal suggested that clays might have played a significant role in primitive earth through the process of concentration and adsorption of the biologically formed biomonomers and thus protecting them against hydrolytic fission.Adsorption of adenine was studied in presence of montmorillonite clay with or without cations Ca^2+,Cu^2+,Mg^2+.Studies carried out have shown that adsorption of adenine was dependent on pH and shows Langmuir adsorption isotherm. Percent binding and values of Langmuir adsorption isotherm on montmorillonite clay with or without divalent cations show that adsorption trend largely depend on the nature of adsorbate and the adsorbent.

Key words: Adsorption, Biomonomers, Chemical evolution,Divalent Langmuir coefficients, Montmorillonite.,Oligomerisation

1. INTRODUCTION

It is assumed that clays minerals and metal oxides available near sea shores or sea beds might have played a key role in concentration of biomonomers through adsorption and desorption processes on their surfaces. The importance of clay minerals in chemical evolution was first suggested by **Bernal[1]** in 1951. and proposed that clays near the hydrosphere-lithosphere interface might have adsorbed micro biomonomers on and between their silicate layers and then facilitating condensation considerably leading to the formation of biopolymers and protecting them against hydrolysis. Lahav and **Chang [2](1976), Paech – Horowitz and Erich[3](1988)** suggested that condensation reactions of precursors of proteins and nucleic acids proceeded under extreme fluctuating environments where rainstorms, flooding, dehydration and freezing occurred and thermal or solar ultraviolet flux played a significant role, giving rise to macromolecules by adsorption of monomers and their subsequent condensation.

Ponnamperuma et al.[4] reviewed the possible role of clays in chemical evolution and suggested that clays are ionically charged surfaces where exchange of inorganic cations for organic cations in solutions take place. Organic molecules are also adsorbed and concentrated on clay surfaces.

Kamaluddin et al. [5] have reported the adsorption of amino acids and nucleotides on transition metal ferrocyanides as possible adsorbents in primitive lifeless era. Ferris and coworkers[6], Lahav at al[7].have reported that clay minerals as insoluble alumino silicates exhibit high adsorption and catalytic capabilities in the process of amino acid and nucleotide polymerization.

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Recently Bujdak and coworkers,[8] Basuik et al[9], Yanagava and Kobayashi[10], have suggested that clays and silicon oxide which were in abundance on the earth crust in remote abiotic times might have catalyzed oligomerisation reactions of amino acids leading to the evolution of fore proteins. Although experiments concerning adsorption of amino acids and their short peptides on solid surfaces under prebiotic conditions have been carried out and reviewed (Kalra et al.2000, [11,]; Meng et al.2004[12]; Zaia,2004 [13]; Whitehouse et al.2005 [14]; Kawamura et al. 2009[15] and Pant et al 2009 [16]). Studies carried out in our laboratory have shown that the adsorption isotherm were dependent on the nature of adsorbate, adsorbent and pH of the suspension. In order to find out the conceivable reason for such vexed pathways, an attempt has been made to study the adsorption of adenine on montmorillonite clay with or without divalent cations (Cu^{2+}, Mg^{2+} and Ca^{2+}) as adsorbent for preferential adsorption under prebiotic conditions believed to have existed near lithosphere-hydrosphere boundary of primitive sea or in sea beds.

2. EXPERIMENTAL:

2.1 Chemicals: - Montmorillonite (Smectite group of clay) was purchased from Aldrich Chemical Co. Adenine from Sigma Chemical Co. All other chemicals were of analytical grade. The stock solution of adenine (7×10^{-5} M) was prepared in deionised water obtained after triple distillation in an all glass assembly. For preparation of solutions/regents and experimentation,de ionised water was used after double distillation in an all glass assembly. A Jasco, V-550, UV/Vis spectrophotometer was used for determination of absorbance . pH was recorded on Agronic digital pH meter-511.

2.2 Preparation of cation exchanged montmorillonite clay: Cation exchanged (Ca^{2+}, Cu^{2+} and Mg^{2+}) montmorillonite clay used were prepared by saturation method . Saturated solutions of respective chloride (i.e. $CaCl_2$, $CuCl_2$, $MgCl_2$) were prepared and montmorillonite clay was added to this saturated solution with constant stirring. The mixture was kept at room temperature for 8 hrs and then excess of the salts were leached out by washing with distilled water until it was freed from chloride ion. The divalent cation exchanged forms thus obtained were dried at room temperature and kept in vacuum dessicator.

2.3 Spectral Studies:- The electronic spectra of adenine were recorded using Jasco,V-550,UV spectrophotometer and their characteristic values of λ_{max}. at pH 7.2.

2.4 Adsorption Studies:- Adsorption experiments of adenine were carried out with montmorillonite clay and cation exchanged clays in triple distilled water. The concentration of the reaction solution after adsorption were recorded by using Jasco,V-550 UV spectrophotometer and pH was measured in a digital pH meter. Montmorillonite was repeatedly washed with distilled water and dried at 25°C before use. Adsorption of adenine was studied as a function of pH and concentration of adsorbate. Therefore, adsorption of adenine in varying concentrations ($7 \times 10^{-5} - 2.0 \times 10^{-5}$M) on montmorillonite and cation exchanged clays over a pH range 3.6-9.2 was studied by adding appropriate buffer to 5 ml solution of adsorbate in order to obtain saturation point. Acetate buffer (0.2N acetic acid and 2N sodium acetate) and borax buffer (0.2M boric acid and 0.05 M borex) were used to maintain pH in the range 3.6-5.5 and 6.8-9.2 respectively. Buffered solution of adsorbate (5ml each) was added to montomorillonite /cation exchanged clay (50mg each) in separate ground glass conical flask (50ml). The flasks were capped and the content were stirred mechanically for 20 min. These were allowed to stand at room temperature for 8hrs. Similar sets adenine(nucleic acid base) were incubated at different temperatures and pH to find out the condition of maximum adsorption. After about 8 hrs, the experimental solution containing different adsorbents were centrifuged at 3000 rpm for 15 minutes. The concentration of all adsorbates used were determined by UV spectrophotometer at wavelength of maximum adsorption of respective adsorbate. The amount of adsorbed adenine were calculated by the difference between the concentration of respective adsrobate before and after adsorption. The equilibrium concentration of adsorbates and the amount adsorbed were used to obtain the adsorption isotherm. The adsorption parameters X_m and K_L were calculated from the slope and the intercept obtained from the graph of C_{eq}/X_e versus C_{eq}. The values are summarized in table 01. X_e was calculated asymptotically from figs. B and C. on extrapolating the adsorption curve towards Y-axis when saturation phenomenon occurs.

3.RESULTS AND DISCUSSION:

The adsorption of adenine on Montmorillonite clay and cation exchanged clay in aqueous medium was studied as a function of pH (3.6-9.2), temperature (25° -35° C) and concentration($7 \times 10^{-5} - 2.0 \times 10^{-5}$M) of the adsorbate in order to find out the conditions of maximum adsorption. Moreover, the main aim is to study the adsorption of adenine on montmorillonite clay with or without divalent cations (Cu^{2+}, Mg^{2+} and Ca^{2+}) as adsorbent for preferential adsorption under prebiotic conditions believed to have existed near lithosphere-hydrosphere boundary of primitive sea or on the bottom of the sea. The study of adsorption as a function of temperature showed maximum adsorption at 25°C. Preliminary studies have shown that the amount of adenine adsorbed on Montmorillonite clay separately were dependent on the pH of the solution and it was maximum at pH 7.2 (Fig.A). Subsequent studies were therefore carried out at 7.2 for adenine in all cases studied related to the adsorption. However, interaction of clay and metal ion co-ordinated clays depend on some factors like ionic strength or orientation at sites for interaction with clay surface. Incorporation of metal ions on clay increases the cationic strength of montmorillonite surface and thus lowers the repulsive forces between adenine and clay surface. The results recorded in table 01 show an increase in percent binding in presence of cation incorporated clays. The equilibrium concentration of adenine and the amount adsorbed per gram of adsorbent were used to obtain the adsorption isotherm (Fig B & C). From the figures it appears that the amount of adenine adsorbed increases as their equilibrium concentration increases in solution becomes independent of the concentration. Initially, the curve shows linear relationship between amount adsorbed and equilibrium concentration, whereas at higher concentration, saturation point occurs and no adsorption takes place. The asymptotic nature of adsorption isotherm suggested Langmuir type adsorption or monolayer formation as given below :

$$Ceq / Xe = 1/K_L.Xm + Ceq / Xm$$

Ceq = Equilibrium concentration of amino acid
K_L = Constant related to the heat of adsorption or enthalpy
Xe = Amount of adsrobate (mg) adsorbed per gram of adsorbent
Xm = Amount of adsrobate required for per gram weight of adsorbent for forming a complete monolayer on the surface.

It was observed that adsorption trend (% binding, values of Langmuir constants) of adsorbate adsorbed on montmorillonite clay (M) with or without cations largely depend on the nature of adsorbate as well as adsorbent. Results of adsorption of adenine are recorded in table 01. in terms of percent binding. Percent binding has been calculated with the help of optical densities of respective biomonomer solution before and after adsorption corresponding to saturation point on the curves. The percent binding of adenine appear to have the following order:

$M\text{-}Mg^{2+} > M\text{-}Cu^{2+} > M\text{-}Ca^{2+} > M$

The effectiveness of various adsorbents with divalent cations towards the adsorption of adenine was found as follows:

$M\text{-}Ca^{2+} > M\text{-}Cu^{2+} > M\text{-}Mg^{2+} > M$
(where, M stands for Montmorillonite clay)

Thus the addition of Mg^{2+}, Cu^{2+}, Ca^{2+} increases the adsorption throughout the entire concentration range of the isotherms. This shows that the increase in ionic strength of clay, increases the attractive force between the adenine and clay surface. On the basis of the observations, the main role of inorganic cations in the adsorption on clay may be accounted as the neutralization of the negatively charged surface of the clay by intercalation of divalent cations in between. The X_m values recorded in table 02 reveal that the effect of metal cations incorporated clay on adsorption of adenine for monolayer formation was relatively significant . The divalent metal cation acts as a bridge in between the two negative charges and thus due to higher electrostatic forces of attraction, the complex becomes stable in the aqueous environment of primitive sand beds.

Table-1

Percent binding of adenine on Montmorillonite clay(M) with or without divalent cations.

Amino acids	M	M-Ca^{2+}	M-Cu^{2+}	M-Mg^{2+}
Adenine	54	57	58.7	61

$$\text{* \% binding} = \frac{\text{Conc. before adsorption - Conc. after adsorption}}{\text{Conc. before adsorption}} \times 100$$

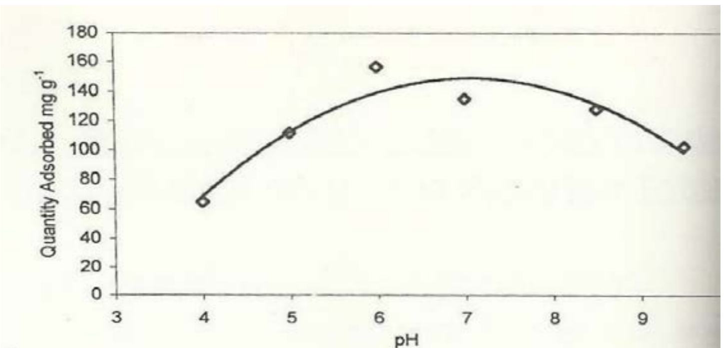

Fig. A Adsorption of adenine on montmorillonite clay(M)as a function of pH ;temperature 23°C

Table -2

Langmuir constants for adsorption of Adenine on Montmorillonite clay(M) with or without divalent cations.

Types of adsorbents	Langmuir constants Adenine		
	Xm (mg/g)	K_L ($L mg^{-1}$)	r^2
M	118	-181.58	0.9999
M-Ca^{2+}	158	-67.28	0.9999
M-Cu^{2+}	140	-65.21	0.9999
M-Mg^{2+}	130	-146.86	0.9999

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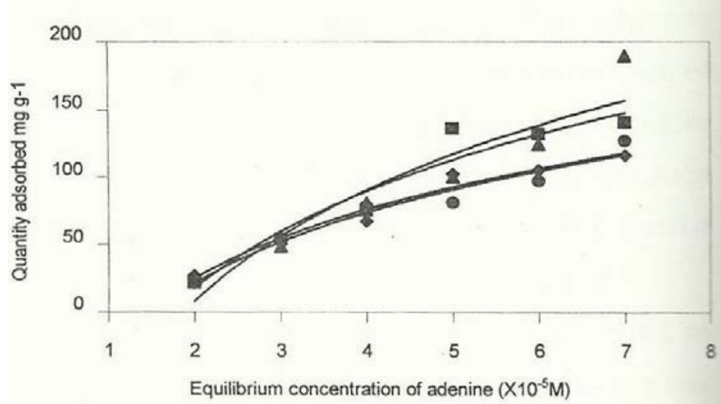

Fig. B Adsorption isotherm of adenine on montmorillonite clay (M)with or without cations

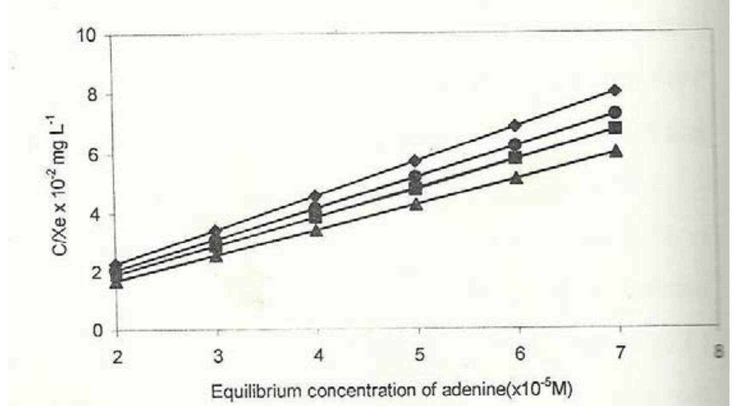

Fig. C Langmuir adsorption of adenine on montmorillonite clay(M) with or without cations, pH 7.2; temp.25°C

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