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Research paper

Role of preparation method on the extent of montmorillonite catalysis for oligomer formation

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ABSTRACT

The extent of catalytic activity of montmorillonites (Mts)[1] for RNA-like oligomer synthesis varies considerably depending on the method used to prepare the Mt. Homoionic Mt prepared by titration method produced longer oligomers with higher yields compared with Mt prepared by saturation method. The difference in catalytic activity between these two types of Mts is related to the difference in nature of their edge sites.

1. Introduction

In his lecture delivered in 1947, John Bernal (1949) put forward his hypothesis stating that minerals may have served as catalyst for the formation of biomolecules in processes leading to the origin of life by adsorbing their organic precursors on their surfaces, thereby bringing them into a favorable orientation for reactions to occur, and also protecting these adsorbed molecules from the destructive effects of UV and gamma radiation. A few decades later, Lohrmann (1977) demonstrated that activated monomers of RNA (ribonucleic acids), one of the three building blocks of life, along with DNA (deoxyribonucleic acids) and proteins, may have formed under potentially prebiotic conditions. He reacted a solution of 0.05 M adenosine 5′-triphosphate, ATP, with 0.625 M imidazole solution under plausibly prebiotic conditions, i.e., at ambient temperature and humidity, and obtained activated monomers of 5′-adenosine monophosphate, ImpA.

In the light of this information, Gilbert (1986) put forward his RNA World Hypothesis in which he claimed that RNA may have formed by the polymerization of its activated monomers present on the primitive Earth.

To test Bernal's and Gilbert's hypotheses, we studied the reaction of activated forms of 5′-adenosine monophosphate (ImpA) and 5′-cytidine monophosphate (ImpC) (Fig. 1) in the presence of montmorillonite (Mt) used as a catalyst.

High-performance liquid chromatography (HPLC) analysis of the products demonstrated that Mt catalyzed the reaction of activated monomers, producing oligomers containing 10–12 monomer units in their chain (Ertem and Ferris, 1996; Ferris and Ertem, 1992). The oligomerization reaction takes place in the interlayer of Mt (Ertem and Ferris, 1998). It is therefore not surprising that the extent of catalysis, that is, the number of monomer units joined together to form the oligomer chain, and their yields vary considerably with the nature of interlayer cation, purity of the activated monomer (Ertem, 2004 and references therein), and charge density of Mt (Ertem et al., 2010).

The procedure followed to prepare the homoionic Na^+–Mt from Volclay has a significant effect on the oligomer length and yields: Na^+–Mt prepared by the titration method (Banin et al., 1985) produced oligomers containing ten or more monomer units in their chain, whereas Na^+–Mt prepared by a batch saturation method catalyzed the formation of oligomers containing up to five monomer units in very low yields, Table 1.

This work was designed to determine the reason(s) for the differences in extent of catalytic activity of homoionic Mts prepared by different exchange methods.

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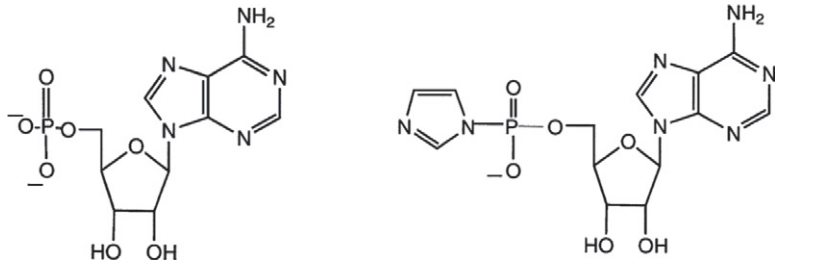

5'-Adenosine monophosphate (5'-AMP)

Activated 5'-Adenosine monophosphate (ImpA)

Fig. 1. Structures of 5′-adenosine monophosphate and its activated form.

2. Experimental

2.1. Materials

Mt, Volclay SPV 200, was provided by the American Colloid Company, Arlington Heights, IL. The structural formula derived from its chemical analysis (Brindley and Ertem, 1971) is:

$$Na_{0.33}\left[Al_{1.57}Fe^{3+}{}_{0.17}Fe^{2+}{}_{0.02}\,Mg^{2+}{}_{0.27}\right]^{VI}\left[Si_{3.89}Al_{0.11}\right]^{IV}O_{10}(OH)_2.$$

All reagents and solvents were purchased from SIGMA. HPLC analysis was performed using an Alltima HEMA-IEC BIO Q anion-exchange column from Alltech. Doubly distilled water was used for all experiments.

2.2. Preparation of Na^+–Mt by the titration method (Banin et al, 1985)

Freshly prepared H_3O^+–Mt by stirring the clay mineral with 0.5 M HCl at 4 °C was titrated with NaCl solution in the presence of OH^--saturated anion-exchange resin. The titration method involved adding 0.5 M NaCl solution to an H_3O^+–Mt suspension under constant stirring with a mechanical stirrer to avoid breaking the resin particles. Na^+ ions replaced the interlayer H_3O^+ ions and Cl^- ions exchanged with the OH^- ions on the resin. The H_3O^+ and OH^- thus formed neutralized each other. Titration was usually terminated at a pH of ~5.5. Towards the end of titration, 0.1 M NaCl solution was used to approach the desired pH value more steadily.

$$H_3O^+\text{-Mt} + \text{Resin-OH} + Na^+ + Cl^- \rightleftharpoons Na^+\text{-Mt} + \text{Resin-Cl} + H_2O.$$

2.3. Preparation of homoionic Na^+–Mt by saturation method (Brindley and Ertem, 1971)

Volclay was shaken with a 1 M NaCl solution for 24 h, centrifuged, and the supernatant was discarded. This procedure was repeated two more times and the excess NaCl was removed by shaking the mixture several times with water followed by centrifugation until the supernatant was free of chloride ions when tested with 0.1 M $AgNO_3$ solution. Complete removal of NaCl was accomplished by washing three more times, and the <2 μm particle size fraction was separated by a final centrifugation. The dispersion was subsequently dialyzed against water and was freeze-dried before use.

2.4. Synthesis of activated monomers, ImpA or ImpC

Experiments were carried out under argon atmosphere using an argon-filled balloon fitted with septa, and all the solvents were kept over molecular sieves to keep them water free. Dipyridildisulfide (ATRIOL), triphenylphosphine, and triethyl amine were added to a mixture of 5′-Adenylic acid (adenosine 5′-monophosphate) and imidazole, which was then dissolved in a mixture of dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF). The resulting mixture was magnetically stirred at room temperature for 2 h and then transferred into a flask containing dry acetone, diethyl ether, and triethyl amine. After stirring the mixture for 2 h, the product was converted to its sodium salt by stirring it with $NaClO_4$ in acetone. ImpC synthesis followed the same procedure starting with 5′-CMP (cytidylic acid) instead of 5′-AMP.

2.5. Oligomerization of ImpA by Mt catalysis

1.0 mL of freshly prepared 0.014 M ImpA (or ImpC) solution prepared in 0.2 M NaCl and 0.075 M $MgCl_2$ was added to 50 mg of Na–Mt prepared by either the titration method or the saturation method in a 2 mL polypropylene centrifuge tube. Mixtures were vortexed for 30 s, allowed to stand for three days at 25 °C, and then centrifuged. The supernatants containing the oligomerization products were removed after centrifugation and were held at −20 °C until analysis.

2.6. Analysis of reaction products

Oligomerization products were analyzed by HPLC using an anion-exchange column, which separates components according to their charge. As the number of monomer units in the oligomer chain increases, the elution time also increases. Therefore, unreacted monomer and short oligomers eluted from the column with shorter retention times compared with longer oligomer chains (Fig. 2). The oligomer distribution and their yields are listed in Table 1. Yields of the products were calculated as the area percentage of each peak on the chromatogram and were not corrected for hyperchromicity.

Table 1
Comparison of oligomer yield and lengths formed in the presence of Na^+–Mt prepared by titration and saturation methods.

Preparation method	Number of monomer units in the chain									
	1-mers	*2-mers*	*3-mers*	*4-mers*	*5-mers*	*6-mers*	*7-mers*	*8-mers*	*9-mers*	*10-mer*
Na-Vol (Titr)	29	25	18	14	5.6	3.2	1.5	0.90	0.45	0.24
Na-Vol (Sat)	76	12	2.2	0.40	0.05					