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STEREOSELECTIVITY OF MONTMORILLONITE IN THE ADSORPTION AND DEAMINATION OF SOME AMINO ACIDS

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ABSTRACT: Optical isomers deamination of L- and D-glutamic and aspartic amino acids and of their DL racemic mixtures has been achieved in the presence of Na-montmorillonite at pH = 6 and room temperature. The adsorption curves showed that the enantiomer adsorbed depends on the type of amino acid. Nevertheless, deamination reaction kinetics brought about a stereoselectivity of the clay mineral for the L-isomer and implicitly showed an unquestionable "structural chirality character" of the clay mineral.

Since Bernal's hypothesis (1949) on the possible implication of clay minerals in the origin of life, several investigators (Paecht-Horowitz *et al.*, 1970; Cairns-Smith, 1974, 1975, 1985; Lahav *et al.*, 1978; Coyne *et al.*, 1981; Coyne, 1985; Yamagishi, 1981, 1982, 1983) have attempted to understand the action of clay minerals in the transformation and evolution of organic and bio-organic matter. Many investigators showed that the swelling clay minerals, especially montmorillonite, would be able to assume the role of a pseudo-enzyme (Mortland, 1984; Siffert & Naidja, 1987; Naidja & Siffert, 1989, 1990). The question which persists concerns the stereoselectivity of clay minerals in biochemical reactions, and in particular that raised by Degens *et al.* (1970) as to the cause of the L homochirality of amino acids in living organisms. It is necessary to note that organisms generally contain amino acids in their L-enantiomer form (Lavollay, 1980).

Degens *et al.* (1970) reported a remarkable finding in connection with clay minerals, namely, that L,D- and D,L-aspartic acids in aqueous solution were polymerized at 90°C to differing extents by the catalytic action of kaolin. Thus the L-enantiomer was reported to polymerize to the extent of 25% and the D-isomer to the extent of only 3%. The authors concluded that an asymmetric synthesis of polypeptides had been accomplished on the clay surface and that polymers containing L-amino acids were formed preferentially to those containing D-enantiomers. A later report by Jackson (1971) purported to confirm these asymmetric polymerization findings, to show that the polymerization of aspartic acid failed to occur in the absence of kaolin as catalyst. Jackson also reported that L-phenylalanine was adsorbed by kaolinite to a higher extent than D-phenylalanine. In contrast to these observations, Bonner & Flores (1973) could find no evidence for the differential adsorption of D- versus L-phenylalanine by kaolin from either pH = 6 or pH = 2 solutions, using optical rotatory dispersion, gas chromatography and thin layer chromatography. However, optical rotatory dispersion measurements are unfortunately approximately within the experimental error of the observed rotations.

Similar attempts by Flores & Bonner (1974) on the preferential polymerization of L- over D-aspartic acid under the influence of kaolin also gave negative results. The recovery of unpolymerized D,L-aspartic acid after treatment using kaolin for eight days was essentially quantitative (≈98·1%) suggesting only trivial (if any) polypeptide formation. McCullough & Lemmon (1974) were also unable to confirm that kaolinite catalyses the polymerization of aqueous D- and L-aspartic acid at different rates. No induced optical rotation was found in the reaction solution. Aspartic acid is adsorbed by kaolinite, but no selectivity for one or the other enantiomer was observed. More recently, Bondy & Harrington (1979) observed that L-leucine, L-aspartate and D-glucose bound to bentonite in a stereospecific manner to a much greater extent than did the homologous compounds that are rarely found in nature (D-leucine, D-aspartate and L-glucose). The difference in behaviour is explained by a difference in the properties when the molecules are covalently bound to, or complexed with, other molecules that are themselves chiral. These results appeared doubtful to Youatt & Brown (1981) who demonstrated that the observations of Bondy & Harrington can be explained better in terms of the effects of the binding to bentonite of the products of radiochemical decomposition. The absence of selective adsorption of protein amino acids over non-protein amino acids by Na-montmorillonite was also observed by Friebele *et al.* (1980). The one different observed in the adsorption from the mixtures was a three- and four-fold greater adsorption of β- and γ-amino acids than their α-amino acid counterparts under acidic and neutral conditions. This suggests that clays may have a different role in chemical evolution than previously envisaged. Clays may remove non α-amino acids from solutions and leave α-amino acids in solution to react.

In this respect, Cairns-Smith (1975) considered that the specificity for L- and D-enantiomers would depend on a genetic material (pre-deoxyribonucleic acid) formed at the contact of the clay mineral. Clay minerals which themselves are not constituted by chiral structural units should nevertheless be able to exhibit a chiral character due to the stacking of their structural units.

In order to attempt to answer this question, we examined the adsorption and the deamination reaction of L- and D-enantiomers of glutamic and aspartic acids and of their DL racemic mixtures. These two amino acids play an important role in living organisms, especially in the transport and removal of toxic ammonia. The deamination reaction of glutamic acid in the presence of Na-montmorillonite has already been studied in the laboratory (Naidja & Siffert, 1989). We especially showed that it transforms into α-hydroxyglutaric acid (reaction 1).

$$\begin{array}{l} HOOC\text{–}(CH_2)_2\text{–}CH\text{–}COOH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad NH_2 \end{array} \xrightarrow[\text{aqueous}]{\text{clay}(H_3O^+)} \begin{array}{l} HOOC\text{–}(CH_2)_2\text{–}CH\text{–}COOH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad OH \end{array} + NH_4^+ \quad (1)$$

It is recalled that the deamination reaction in living cells is catalysed by the enzymatic system and principally gives α-ketoglutaric acid, according to the reaction (2)

$$\begin{array}{l} HOOC\text{–}(CH_2)_2\text{–}CH\text{–}COOH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad NH_2 \end{array} \xrightarrow{\text{catalysis}} \begin{array}{l} HOOC\text{–}(CH_2)_2\text{–}C\text{–}COOH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad O \end{array} + NH_3 \uparrow \quad (2)$$

To examine the catalytic activity of clay minerals against the L- and D-enantiomers of glutamic and aspartic acids, the enzymatic system was replaced by a Na-montmorillonite.

MATERIALS AND METHODS

Montmorillonite preparation

The clay used was a montmorillonite from Maghnia (Algeria) and its purification and transformation into the homoionic Na form have already been described by Siffert & Naidja (1987) and Naidja (1988). The chemical composition (in wt%) of the purified sodic clay is:

Si (31·7%); Al (12·3%); Mg (1·61%); Fe (1·2%); Na (1·54%); Ti (150 p.p.m.); Mn (25 p.p.m.).

The cation exchange capacity (CEC) is 67 ± 5 mEq/100 g of the calcined clay (1000°C).

Amino acids

The reagents used were of high purity grade from Sigma Biochemical Society (USA):

L, D- and DL-glutamic acid ($HOOC–(CH_2)_2–CH(NH_2)–COOH$)
L, D- and DL-aspartic acid ($HOOC–CH_2–CH(NH_2)–COOH$)

The specific rotatory power of the products was checked using a Laurent polarimeter.

Techniques

For kinetic measurements of ammonia formation, 0·5 g of Na^+-montmorillonite was dispersed in polysulfone flasks containing 25 cm^3 of the different enantiomers (L or D) and/or DL racemic mixture of glutamic acid (respectively of aspartic acid) in aqueous solution (27·2 mmol/dm^3 at pH 3·08). Three drops of chloroform were added to sterilize the medium and the pH of the suspension was then brought to 6·0 by addition of 1 M NaOH. The substrate decomposition under the action of montmorillonite generates NH_4^+ cations (reaction 1) which to a large extent remain trapped in the interlayer space of the clay mineral. The amount of NH_4^+ cations thus formed after a certain time was then determined by addition of drops of a concentrated NaOH solution to the suspension in order to attain pH 12·0. The ammonia released during the preceding reaction was immediately determined by a specific electrode indicative of NH_3 gas of Orion type (after 1 min). A standardization curve was established for every set of measurements. This technique has been applied by Mortland (1984) and Naidja & Siffert (1989).

Adsorption curves of L, D- and DL-glutamic acid and aspartic acid on to Na^+-montmorillonite were established by dosing the nitrogen amount of the amino acid fixed on the clay surface (24 h contact, sterile medium at pH = 6·0 and T = 20°) by the micro-Kjeldahl method (CNRS, Centre d'Analyse, Vernaison, France).

X-ray diffraction (XRD) patterns of clay-organic complexes were recorded using a Philips PW 1009/80 diffractometer with Cu-$K\alpha$ filtered radiation (λ = 0·154 nm) at a tube setting of 20 mA and 40 kV. The clay-amino acid complexes were sedimented on glass plates and dried at 40°C for three days.

Infrared (IR) spectra of the complexes were recorded on self-supporting thin films obtained by sedimentation of clay suspensions. The spectra of pure glutamic or aspartic acids were obtained using KBr pellets at 1% by weight (Beckman spectrophotometer IR 20; 4000–300 cm^{-1}).

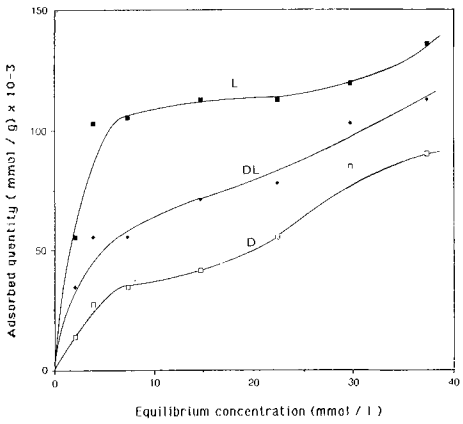

FIG. 1. Adsorption isotherms of L, D- and DL-glutamic acid on to Na^+-montmorillonite at pH = 6·0 and T = 20°C.

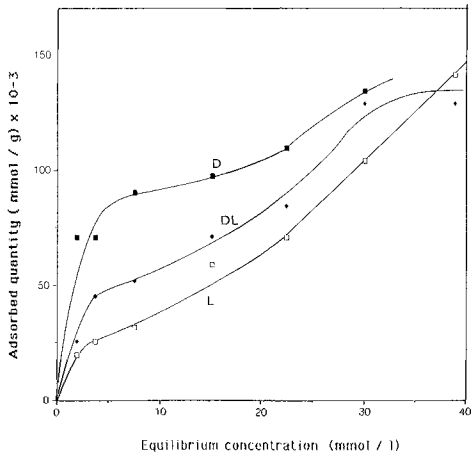

FIG. 2. Adsorption isotherms of L, D- and DL-aspartic acid on to Na^+-montmorillonite at pH = 6·0 and T = 20°C.

RESULTS

Adsorption isotherms

Figure 1 shows that the amino acid amount adsorbed (mmol/g) by the clay at pH = 6 and at room temperature depends on the optical isomer form. Thus, the L-form is rapidly and highly fixed whereas retention of the DL racemic mixture is intermediary. On the other hand, for aspartic acid (Fig. 2), the D-form is better fixed than both the L-form and the racemic mixture.

Ammonia formation kinetics

Another means of ascertaining the "structural chirality" of clay minerals is to study the deamination reaction of the isolated L- and D-enantiomers, and then that of their racemic mixture.

Figures 3 and 4 show that the amount of ammonia formed from the L-enantiomer is clearly higher than that obtained from the racemic mixture and D-form, whatever the amino acid considered. However, it is interesting to notice that the reaction kinetics with glutamic acid are twice that of aspartic acid. It should also be remembered that L-glutamic acid is transformed into α-hydroxyglutaric acid and a small quantity of butyric acid in the presence of montmorillonite (Naidja & Siffert, 1989).

X-ray diffraction

An interpretation of the phenomena became possible on considering the changes of the interlayer spacing of the clay mineral in contact with the L- and D-enantiomer forms of the amino acids. The Na^+-montmorillonite-glutamic acid complexes examined by XRD after sedimentation showed a slight decrease in the interlayer spacing with time (Table 1). This decrease is consistent with a progressive disappearance of the incorporated amino acid. The

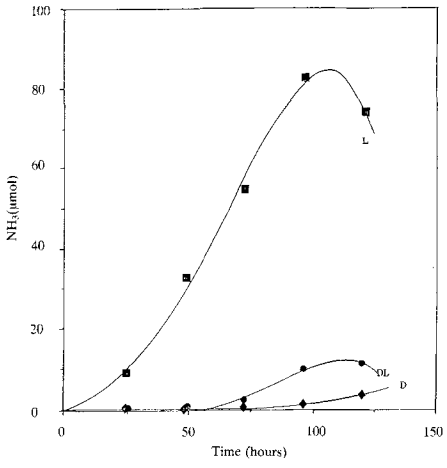

FIG. 3. Kinetics of ammonia formation from glutamic acid at pH = 6·0 and T = 20°C in presence of Na^+-montmorillonite.

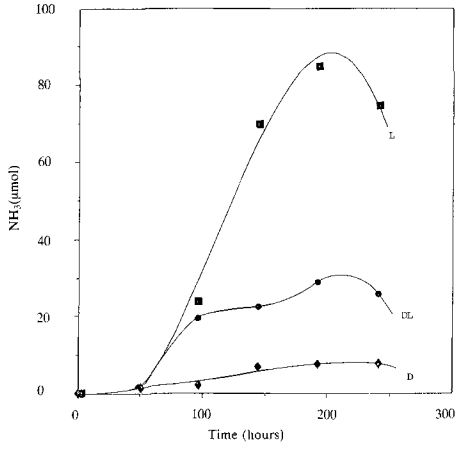

FIG. 4. Kinetics of ammonia formation from aspartic acid at pH = 6·0 and T = 20°C in presence of Na^+-montmorillonite.

interlayer spacing change (Δd_{001}) for the L-form is always higher than that for the other forms (Δd_{001} = 0·46 nm for the L-form, Δd_{001} = 0·45 for the DL racemic mixture and Δd_{001} = 0·39 nm for the D-enantiomer).

The conformation and interlayer ordering of the enantiomer forms are seemingly different. For Na^+-montmorillonite-aspartic acid complexes, the XRD results are difficult to interpret. Different arrangements of the molecules in the interlayer space can be deduced from the XRD patterns on Fig. 5 and it appears that different "stackings" of the adsorbed molecules take place.

Infrared spectra

The Na^+-montmorillonite-glutamic acid complexes were studied by IR spectroscopy after sedimentation, and the appearance of a new adsorption band can be observed at

TABLE 1. Basal spacing d_{001} and change in interlayer spacing Δd_{001} (nm) of Na^+-montmorillonite-glutamic acid complexes (L, D- and DL-forms) sedimented and dried at 40°C (3 days) after different periods of contact.

Time (h)	24	48	72	96	120
Na^+-M^{te}-L-glut.	1·49	1·47	1·44	1·41	1·40
Δd_{001} (nm)	0·46	0·43	0·41	0·37	0·36
Na^+-M^{te}-DL-glut.	1·48	1·45	1·44	1·40	1·38
Δd_{001} (nm)	0·45	0·41	0·41	0·36	0·35
Na^+-M^{te}-D-glut.	1·42	1·40	1·40	1·38	1·29
Δd_{001} (nm)	0·39	0·37	0·37	0·35	0·32

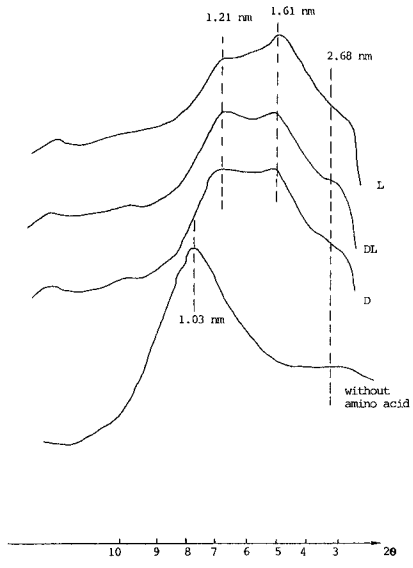

FIG. 5. XRD patterns of Na^+-montmorillonite-aspartic acid complexes after 240 h of contact at pH = 6·0 and T = 20°C, sedimented and dried at 40°C (3 days).

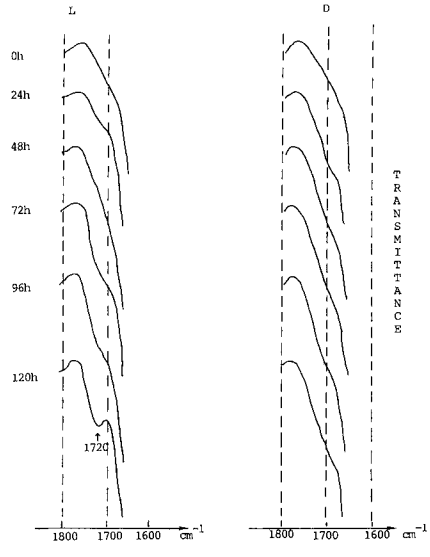

FIG. 6. IR spectra of Na^+-montmorillonite-glutamic acid complexes after different periods of contact of clay and amino acid (L- and D-forms).

1720 cm^{-1} (Fig. 6) attributed to the stretching vibrations of unionized acid groups (COOH). The predominant species of the amino acid at pH = 6 is the zwitterion:

$$^{-}OOC\text{–}(CH_2)_2\text{–}CH(NH_3^{+})\text{–}COO^{-}$$

During the hydrolysis of this ion in the interlayer space of the clay and hydroxyglutamic acid formation, protonation of the ionized acid groups took place (Naidja & Siffert, 1989). The increase of the intensity of the band at 1720 cm^{-1} for the L-enantiomer confirmed the transformation of the amino acid. The same band was hardly visible (only a shoulder could be detected) for the D-enantiomer. More details on the evolution of IR spectra of glutamate-montmorillonite complexes were given by Naidja & Siffert (1989), especially on the progressive increase of the NH_4^+ stretching vibration at ~1430 cm^{-1}.

DISCUSSION

Experimental XRD results show that the stackings of the molecules in the interlayer space are different for the two amino acids enantiomers. Experimentally a higher reactivity of the L optical isomer is observed. Degens *et al.* (1970), Julg (1987, 1988) and Julg & Ozias (1988) interpreted the difference in reactivity of the two forms of optically active molecules in contact with the clay mineral by a "structural asymmetry" of the kaolinite crystal. In fact, there are two crystalline enantiomer forms of kaolinite. Kaolinite which does not have triclinic symmetry stacking of layers, exhibits two inverse forms depending on whether the (a,b,c) trihedron is direct or indirect (forms A and B, respectively). Julg showed by a perturbative quantum treatment introducing the weak nuclear interactions that the form A is slightly more stable than the form B, and consequently more abundant (~10^{-6}). Yet, Julg (1987) pointed out from calculations that the difference in behaviour of L- and D-alanine enantiomers towards kaolinite is due to this "structural asymmetry".

A stereoselective adsorption of optically active molecules by kaolinite, therefore, becomes understandable, but there is still confusion in the literature. Bonner & Flores (1973), Flores & Bonner (1974) and McCullough & Lemmon (1974) did not observe any selective adsorption (or polymerization) of amino acid enantiomers by kaolinite. Similar results seem to be obtained with bentonite (Bondy & Harrington, 1979).

In our studies using montmorillonite, no "structural asymmetry" is possible. Statistically, the crystal structure of montmorillonite does not display any asymmetry and it cannot be considered as possessing its own "structural chirality". Hence, there is no asymmetric crytallographic form allowing preferential adsorption.

To interpret our results, two hypotheses can be proposed. The first involves consideration of a special distribution of the interlayer cations and acid sites favouring different orientations of the two enantiomer forms in the interlayer space.

Ponnamperuma *et al.* (1982) thought that some type of asymmetry might result from the distribution and arrangement of octahedral vacancies, in which Al^{3+} is replaced by Mg^{2+} in the structural layers of the clay. Thus an occasional chirality might result from the arrangement and frequency at cation exchange sites on the two facing silica tetrahedral sheets. It is well known that the molecular intercalation may be accompanied by a specific orientation of the molecules against the sheets (Theng, 1974).

We showed (Naidja & Siffert, 1989) that at pH = 6·0, glutamic acid is mainly in the shape of:

$$^{-}OOC\text{–}(CH_2)_2\text{–}\underset{\displaystyle NH_3^{+}}{\underset{|}{CH}}\text{–}COO^{-}$$

Therefore amino acid intercalation, its protonation and finally its hydrolysis should depend on the orientation of the $-COO^-$ and NH_3^+ groups. Julg (1988) clearly showed that amino acid molecules might assume different orientations at the external surface of kaolinite. In the interlayer space, the problem obviously becomes more complicated.

The second hypothesis is that of Yamagishi (1981, 1982, 1983, 1985, 1987) who suggested a transfer at the mineral surface of an "asymmetry" created by the "stacking" of the optically active ions in the interlayer space. Yamagishi in his study on the adsorption of chelated metallic complexes on Na-montmorillonite showed that clay-chelate metallic complexes substructures can act as selective agents on racemic mixtures. In other words, the "structural chirality" of clays on optically active molecules originates from a different stacking of the metallic complexes in the clay interlayer space. The "structural chirality" would be induced by the adsorbate. According to Yamagishi, the incorporation of the racemic mixture should be favoured because in racemic adsorption the L-isomers easily fit between the D-isomers. Therefore, the amount adsorbed from racemic solution is twice that from solution of a pure enantiomer.

This arrangement of the incorporated molecules should create in the same way a "structural chirality", hence allowing the mineral to adsorb more easily one or other enantiomer form.

In fact, our experimental results are contradictory. While we observe a high adsorption of the D-enantiomer with aspartic acid (Fig. 2), it is the L-enantiomer which is preferentially adsorbed by glutamic acid (Fig. 1). Our results are in line with the discrepancy observed in amino acid uptake cited in the literature. There must be another parameter since the L-form always remains the most reactive in NH_3 formation whatever the amino acid considered (Figs. 3 and 4). This parameter might be the second carboxylic group ($-COO^-$) at the end of the alkyl chain. It might play an important role in the orientation of the incorporated molecules. The "stacking", and therefore the adsorption and reactivity of the molecules, might change with the separation distance of this second carboxylic group with the amino group (chain length). It is likely that a three-dimensional structure with an "active site" like that encountered with protein molecules might intervene.

In order to answer this question completely, it is necessary to construct a one-dimensional electron density map from the (00*l*) X-ray reflections intensities (Fourier summations of (00*l*) reflections, structure factors in the z direction). We hope to re-examine the deamination experiments using a vermiculite giving well oriented films and an adequate series of (00*l*) reflections.

CONCLUSIONS

Experimental results showed a certain stereospecific "recognition" and preference of the Na^+-montmorillonite against the L-enantiomer form of the amino acids. This phenomenon gives rise to higher deamination of the L-form. At present the origin of this "structural chirality" remains unknown. It cannot be due to the presence of two crystalline enantiomer

forms as for kaolinite which allows selective adsorption. A possible explanation may be a different orientation of the incorporated molecule functional groups, i.e., the intermolecular forces between the incorporated molecules would be different for L- or D-enantiomer "stacking". This interpretation is in line with Yamagishi's hypothesis. Only an X-ray analysis giving the electronic density distribution in a direction perpendicular to the sheet would be able to provide a convincing answer.

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