J.Mol.Evol.5,243-247 (1975)

Simultaneous Existence of Different Environments in Aqueous Clay Systems and Its Possible Role in Prebiotic Synthesis

N. LAHAV
The Hebrew University of Jerusalem

Received January 7, 1975; March 31, 1975

Summary. The formation of packets of parallel oriented platelets and separating distances of several angstrom units in montmorillonite-water systems produces an intrinsic inhomogeneity with respect to the proton donating power of internal and external zones. Stable packets can be induced by both inorganic and organic molecules or ions, in suspensions or in drying-out systems. The coexistence of zones with different proton donating power was demonstrated by the pH-sensitive color reaction of benzidine, where stable packets of montmorillonite platelets were formed by the use of either paraquat or diquat.

The close proximity of the two types of zones, which can be of the order of several angstroms, produces the conditions which were defined by Katchalsky as essential for the polymerization of amino acids. Since these environmental conditions are quite common in nature, both at present and in prebiotic times, it is proposed that the inhomogeneity of clay-water systems with respect to proton donating power should be taken into account in both theoretical and experimental efforts to demonstrate the catalytic activity of clays in prebiotic synthesis.

Key words: Surface (Interlayer) Acidity - Montmorillonite - Benzidine

Bernal (1951) was the first to suggest that prebiotic synthesis may have taken place on clay particles in aqueous media, where they simultaneously protected the prebiotic monomers from photolytic degradation and provided a catalytic region for the promotion of subsequent polymerization and chemical development. More recently Cairns-Smith (1966) has suggested that clay minerals might have been additionally implicated in the origin of the most primitive genetic code, through replicating crystal imperfections.

Several investigators have studied the catalytic polymerization of amino acids and purine bases into complex macromolecules such as polypeptides, induced by clay minerals (see the recent reviews by Fripiat & Cruz-Cumplido (1974), Anderson & Banin (1975), Calvin (1974), Good (1973), and Katchalsky (1973). Anderson & Banin (1973, 1975) have indicated the ability of expanding clays to affect the orientation and positioning of reactant molecules, where ordinary phenomena such as flocculation, wetting and drying, or freezing and thawing, have a great influence on these processes. In particular, it is interesting to quote Katchalsky (1973) in connection with his efforts to define the environmental conditions necessary for the polymerization of amino acids: "What we were looking for were aqueous conditions at a pH very close to neutral and at a temperature close to room temperature which would make the amino acids behave as if they were at a very low pH". In the following discussion it will be shown that these environmental conditions are quite common in nature, both at present and in prebiotic times.

It is now well established that the proton donating properties of partially dehydrated clay surface are greater than would be expected from pH measurements of clay in water and that this tendency increases as the water content decreases (Fripiat & Cruz-Cumplido, 1974; Mortland & Raman, 1968; Touillaux et al., 1968). This effect, sometimes called "surface acidity" or "interlayer acidity", was explained by Mortland & Raman (1968) as the result of polarization effects when the exchangeable cations become more concentrated on the fewer remaining water molecules. It is not necessary for the whole clay-water system to be evenly dried in order to obtain the interlayer acidity: when the clay unit-layers are closely packed to form tactoids or "packets" of parallel oriented platelets there may be considerable interlayer acidity inside these packets even when the bulk solution outside these regions is neutral.

The existence of stable packets made up of the unit layers inside which there is considerable surface acidity can be demonstrated by the use of molecules which bring about stable and parallel association between clay unit layers. Montmorillonite adsorbs very strongly the two bipyridylium herbicides, paraquat[1] and diquat[2] (Weber et al., 1965). Upon drying the basal spacing of montmorillonite-paraquat and montmorillonite-diquat is about 13 A (Weber et al., 1965). These two complexes were formed in aqueous suspensions[3] and then

---

[1] 1,1-Dimethyl-e, 4-Bipyridinium Dichloride. Supplied by ICI.

[2] 6,7-Dihydrodipyrido (1,2-a:2', 1'-c)-Pyrazidinium Dibromide. Supplied by ICI.

[3] The experimental details will be published elsewhere.

dried either at 100°C or by freeze drying. Addition of benzidine solution to the dry montmorillonite complexes produced blue and yellow aggregates which coexisted in the same solution for many days: the color of the small aggregates was blue whereas that of the large ones was yellow green. The pH of the solution was 6.7. The color reaction of benzidine-montmorillonite (Furukawa & Brindley, 1973; Lahav & Raziel, 1971; Theng, 1971) is pH sensitive: the benzidine-blue which is formed on the montmorillonite surface at slightly acid and alkaline conditions is changed into yellow upon adding acid. The yellow color is dominant at pH values below about 3 or so (Dodd & Ray, 1960). The yellow or green colors are formed also upon drying the clay, the color change being ascribed to interlayer acidity (Lahav, 1971; Lahav & Anderson, 1973).

The formation of the yellow and green colors in the aggregates is an indication of the interlayer acidity inside these aggregates. Presumably the yellow quinoidal cation exists also inside the small aggregates but its color is masked by the blue semiquinone cation. The green color formation can be explained either as a combination of blue and yellow colors (Lahav & Anderson, 1973) or another unstable quinoidal form.

It is possible to envisage several natural mechanisms which can bring about the formation and existence of such packets for a considerable length of time; the two which seem most relevant to the conditions favorable for abiotic development (see also Anderson & Banin, 1973) are now explained.

1. Interlinking of Clay Particles. Interlinking of clay particles can be carried out by either organic or inorganic molecules and ions. In Ca-montmorillonite suspensions the basal spacing is fixed at about 19A (except for very high Ca^{+2} concentrations), which corresponds to 3 to 4 H_2O layers (Norrish & Quirk, 1954). It is not known whether considerable interlayer acidity can be developed in the Ca-montmorillonite particles. Basal spacings of ∿12.5A were observed by Lailach et al. (1968) in montmorillonite saturated by several organic molecules and suspended in water. Interlayer acidity in these aggregates is probably considerable.

2. Wetting-Drying Cycles. Though the quantitative relationships between the basal spacing and the intensity of the interlayer acidity is not known, it is obvious that in the borderlines of water bodies, wetting-drying cycles bring about cyclic changes in the interlayer acidity of swelling

clays. The intensity of these changes depends on several factors, such as range of fluctuation of water content, predominant clay mineral, exchangeable cations, and electrolyte concentrations. Hysteresis effects are also expected under these conditions (Blackmore & Miller, 1961; Lahav & Banin, 1968; Quirk, 1968). Since such a natural system is never completely homogeneous, it is expected that packets of clay unit-layers near pores filled with normal solution will be found. Depending on the environmental conditions, such transitional situations can endure for many days, which may be significant for the abiotic synthesis of certain molecules.

Thus, two systems were considered in which an intrinsic inhomogeneity can exist and where the conditions inside clay packets may be very different from those in the bulk solution. Such systems can be looked upon as if they are made of numerous small "islands" (the clay packets) dispersed in a large volume of "normal" solution. The relatively small size of these "islands" is important in every reaction which takes place across the boundary of these entities, i.e., between the packets and the bulk solution. In particular, one should consider the proton-donating properties of the interlayer water molecules of montmorillonite (Fripiat & Cruz-Cumplido, 1974; Mortland & Raman, 1968).

Returning to the problem of the initial development of living forms and to the abovementioned quote of Katchalsky (1973), the systems described here should be considered in explaining abiotic synthesis of molecules of significant biological interest. For instance, in the experiments on the polymerization of amino-acid adenylates in the presence of montmorillonite (Paecht-Horowitz et al., 1970), protonation of proton accepting groups in the interlayer "acid" zones may be an essential step in the polymerization of the amino acids (personal communication from Professor F.R.Eirich and Dr.M.Paecht-Horowitz).

Acknowledgement. The stimulating discussions with Professor F.E.Eirich, Dr.M.Paecht-Horowitz, and Dr.S.Yariv, and the interest and help of Dr.S.Chang, are greatly appreciated.

REFERENCES

Anderson,D.M., Banin,A. (1973). Proc.Fourth Int.Conf. on the Origin of Life, Barcelona

Bernal,J.D. (1951). The physical basis of life. London: Routledge and Kegan Paul

Blackmore,A.V., Miller,R.D. (1961). Soil Sci.Soc.Am.Proc.25,169
Cairns-Smith,A.G. (1966). J.Theor.Biol.10, 53-88
Calvin,M. (1974). Angew.Chem.13, 121
Dodd,C.G., Ray,S. (1960). Clays and Clay Minerals 8, 237
Fripiat,J.J., Cruz-Cumplido,J. (1974). Ann.Rev.Earth, 2, 239
Furukawa,T., Brindley,G.M. (1973). Clays and Clay Minerals 21, 279
Good,W. (1973). J.Theor.Biol.39, 249
Katchalsky,A. (1973). Naturwissenschaften 60, 215
Lahav,N. (1973). Israel J.Chem.10, 925
Lahav,N., Anderson,D.M. (1973). Israel J.Chem.11, 549
Lahav,N., Banin,A. (1968). Israel J.Chem.6, 285
Lahav,N., Raziel,S. (1971). Israel J.Chem.9, 683
Lailach,G.E., Thompson,T.D., Brindley,G.W. (1968). Clays and Clay Minerals 16, 285
Mortland,M.M., Raman,K.V. (1968). Clays and Clay Minerals 16, 393
Norrish,K., Quirk,J.P. (1954). Nature 173, 255
Paecht-Horowitz,M., Berger,J., Katchalsky,A. (1970). Nature 228, 636
Quirk,J.P. (1968). Israel J.Chem.6, 213
Theng,B.K.G. (1971). Clays and Clay Minerals 19, 383
Touillaux,R., Salvador,P., Vandermeersche,C., Fripiat,J.J. (1968). Israel J.Chem.16, 337
Weber,J.B., Perry,P.W., Upchurch,R.P. (1965). Soil Sci.Soc.Amer.Proc.29, 678

Prof.N.Lahav, Acting Head
Department of Soil and Water Sciences,
Faculty of Agriculture, Rehovot, Israel