*Clays and Clay Minerals*, 1972, Vol. 20, pp. 189–191. Pergamon Press. Printed in Great Britain

# NOTE

## Clay-organic complexes

### CLAY-ORGANIC COMPLEXES–A SEMINAR REPORT

A SEMINAR on *Clay-Organic Complexes* was held in Kyoto, Japan, August 24–27, under the auspices of the United States–Japan Cooperative Science Program, administered jointly by the National Science Foundation and the Japan Society for the Promotion of Science. A proposal from the Japanese side that a joint seminar might be of great interest was taken up with enthusiasm in both countries. In addition to the delegations from Japan and the United States, scientists from Germany and Taiwan also participated. E. Suito of Kyoto University and G. W. Brindley of the Pennsylvania State University acted as coordinators, with M. Koizumi of Osaka University as secretary. Some 30 major papers and many smaller contributions were presented. Attention was given mainly to the naturally swelling minerals, smectites and vermiculites, but reactions with kaolinite [6, 22, 26, 30], palygorskite [21], imogolite [4], and calcium silicate [7] also were considered. The seminar was conducted mainly under four broad headings: structures, reactions, experimental methods, and applications.

### STRUCTURES

The structures of clay–organic complexes cannot usually be treated by the precise methods of three-dimensional X-ray diffraction analysis [9, 13]; neither the minerals nor the resulting complexes are sufficiently regular for this type of analysis, but one example (that of 6-aminohexanoic acid vermiculite) was discussed in which sufficient order was obtained to permit conclusions to be drawn [10]. Generally a combination of techniques may lead to valuable results, particularly one-dimensional diffraction analysis combined with quantitative absorption data and i.r. absorption spectrometry [9, 14, 23]. The possibility of using high-resolution electron microscopy for direct observation of individual clay particles and their internal structure, including observations of dislocations and other possible imperfections [11, 13], and for the study of surface reactions (epitaxial processes) [12] was beautifully illustrated; lattice images of octadecylammonium montmorillonite were shown. New data on the effect of temperature on long chain aliphatic complexes of montmorillonite were brought forward. It has been known that chain molecules can take up different orientations at temperatures above and below their normal melting points. The new data showed that kink formation occurred [15]; as the melting point was approached, the basal spacing decreased in small steps, at the melting point a much larger decrease occurred, and above the melting point further small decreases took place. The detailed results were complex and montmorillonite with a very uniform charge distribution was said to be necessary to observe these effects [15].

### REACTIONS

Reactions between clays and organic materials [3–7] was probably the major topic of the seminar, and i.r. spectroscopic analysis is the most widely applied technique. From the pleochroism of critical vibration frequencies, the orientation of organic molecules relative to the silicate layer structure in favorable cases may be unequivocally determined [9, 14, 23]; this requires that the assignment of the i.r. frequencies be known and that the organic molecules take up clearly defined arrangements. Spectral frequency shifts or absence of such shifts may indicate the presence or absence of interactions involving particular functional groups [3, 14].

Absorption of organic molecules as a result of protonation occurs in a variety of ways [3]. Cation exchange of inorganic by organic cations is well known. In partially exchanged systems, a segregation may occur of the two kinds of cations in different layers, with the formation of interstratified structures. Besides external protonation, internal protonation can occur by various mechanisms: (i) by $H^+$ ions occupying exchange sites, (ii) by dissociated water molecules associated with metal cations, (iii) by proton transfer from another cationic species already present. An acid clay surface is quite acidic and molecules such as amines, urea and amides are readily protonated within the layer structure. Water, particularly in trace amounts in montmorillonites containing cations with high electric fields, may be highly dissociated and a proton may be donated to an organic molecule or may serve as a "bridge" between the cation and the organic molecule. When the amount of an absorbed base exceeds the protons available for cation formation, the additional organic may be held as neutral molecules, or a strong symmetrical hydrogen bond of the type ($B \cdots H^+ \cdots B$) may be formed.

Another class of complex involves cation-dipole reactions between the inorganic cations and dipole groups of the molecules. A particularly interesting type of complex was described [3] between aromatic molecules (such as benzene and variously substituted benzenes) and $Cu^{2+}$ ions through the $\pi$ electron system of the organic molecules.

The trimethylsilation of calcium hydrous silicates by the Lentz method (reaction with an organo-silicon compound such as hexamethyldisiloxane) was described using hydrothermal reactions under conditions which would produce tobermorite gel, crystalline tobermorite or xonotlite [7]. The nature of the products, linear or ladder-type polymers, was shown to depend on the crystalline state of the calcium silicate.



https://doi.org/10.1346/CCMN.1972.0200312 Published online by Cambridge University Press

## CLAY MINERALS AS CATALYSTS

The role of clay minerals as catalysts in organic reactions was discussed in several papers. The possible role of clays as high surface area adsorbents in the synthesis of biochemically important molecules[18] in prebiotic earth history was discussed, and experiments were described in which the various steps in the sequence

$$CO_2 + NH_3 \rightleftharpoons \text{urea} + H_2O \rightleftharpoons \text{amino acids} \rightleftharpoons \text{polypeptides} + H_2O$$

had been studied. The successful synthesis of sugars, cytosine and uracil from $CO_2$ and $NH_3$ in the presence of kaolinite was reported. Clay minerals act as template catalysts for esterification reactions of fatty acids in water to form glycerides. The synthesis of phospholipids using clays as catalysts also was described. This type of mechanism for the formation of complex materials of the kind found in living systems was considered to be a challenging alternative to syntheses in which u.v. radiation, ionizing particles, or electric discharges are used as activating agents.

Clays as catalysts in the genesis of petroleum hydrocarbons[19] was another topic of considerable interest. Chemical kinetic studies indicate that under the diagenetic conditions in sediments when montmorillonites are converting to illites, fatty acids associated with the montmorillonite may be converted to long-chain paraffins, but not immediately to the association found in nature. At greater depths further diagenesis may lead to cracking of the long-chain paraffins resulting in an association similar to that found naturally.

A novel contribution considered the explosiveness of benzoylperoxide[20] mixed with bentonite in the presence of sulphurous acid and its possible application to smog control by spraying benzoylperoxide-silicate dusts over large towns having problems with sulphurous fumes.

## KAOLINITE COMPLEXES

Surface activity and organic adsorption on kaolinite were the subjects of several papers. Adsorption isotherm studies with anhydrous butylamine show strong adsorption in proportion to edge area with one $BuNH_2$ molecule per silanol group, and it appears that the quantity adsorbed is twice as great from non-aqueous (e.g. heptane) as from aqueous solutions[6]. If a hydrate molecule, $BuNH_2 \cdot H_2O$ is adsorbed then steric hindrance may explain the smaller adsorption from aqueous solutions. Another contribution[22] compared the surface modifying effect of butanol on silica gel and on kaolinite. Silica gel becomes hydrophobic by the reaction

$$-OH + C_4H_9OH \rightarrow -OC_4H_9 + H_2O.$$

In the case of kaolinite a decrease in the heat of wetting on immersion in water is small, so that the silanol groups in kaolinite are considered to be less reactive. Halloysite, by contrast, appears to have a more reactive surface than kaolinite.

## EXPERIMENTAL METHODS

Adsorption isotherms for organic compounds are used in a variety of ways for determining surface areas and surface charge and both external and internal areas can be probed[8]. Many points of detail are involved and a clear interpretation of results is not always feasible. Adsorption is studied more often from the liquid phase or from solution than from the vapor phase. Interpretation of solution data becomes uncertain when adsorption of solute and solvent are competitive, as is often the case with solutions of polar organic compounds in water. Surface area determinations involve considerations of monolayer coverage, molecular cross-sectional areas, and packing of molecules on surfaces. If adsorption takes place by cationic replacement, then the spacing of the exchange sites in relation to molecular size becomes an important consideration. The use of methylene blue for determining both surface area and surface charge was discussed.

The design of a calorimeter for measuring the small energy changes in the wetting of clays and in ion exchange reactions was described which involved measuring the off-balance of a bridge circuit incorporating a thermistor [16].

The use of thin clay-organic films in controlled atmospheres for i.r. analysis was described[23]. The use of mass isotopes, particularly of hydrogen, is often very useful in i.r. studies. Differential spectrophotometry is possible by placing thin clay films on two silica discs, with the organic complex developed on one film and with one disc in each beam of the spectrometer.

Other techniques described involved the use of an electron-probe analyser[17] and of a differential refractometer[31], the latter providing a convenient method for following changes of organic concentrations in solutions.

## APPLICATIONS

Many applications of clay-organic complexes depend on the nature of the clay surfaces and on the particle interaction forces after sorption of organic molecules. A systematic treatment[21] distinguishes the effects of small and large organic molecules, and of cationic, anionic and polar compounds, and these were briefly reviewed. Adsorption of organic cations from aqueous solutions condenses the electrical double layer and colloidal stability is decreased. Beyond the equivalence point, additional cations may be physically sorbed with the cationic groups now pointing towards the water phase. There is a reversal of surface charge and colloidal stability may be re-established. Around the equivalence point, the clay surface is preferentially wetted by oils and the emulsifying property of the organic complex is at a maximum. Anionic and polar molecules give rise to different phemomena which were reviewed and contrasted with those developed by cationic molecules.

On the basis of the foregoing considerations, a survey of clay-organic applications was presented[24] under the following headings: interlayer swelling, surface adsorption, modification of wetting properties, peptization by anionics, protective action of polymers, sensitization of polymers. Surveys[27, 28] based on usage dealt with greases and lubricants, cosmetics, drilling muds, foundry sands, adhesives, paints, inks, rubber compounding, vapor phase chromatography. The remark was made that individual applications may be small in volume but are high in quality[24].

A number of specific applications were considered.

https://doi.org/10.1346/CCMN.1972.0200312 Published online by Cambridge University Press

Japanese-produced quaternary ammonium bentonites were described in which both aliphatic ammonium salt and a fatty acid salt were used [25]. Complexes between clays and dyes to be used as pigments were shown (bright red, yellow and blue) but they were said to be weak against light and weather [25]. Complexes made from clays and unsaturated polyesters were described and said to have possible applications as materials for good thermal resistance and good mechanical and thermal properties; potential uses as building and furniture materials were mentioned [25].

The sagging rate of paint films on a vertical surface was discussed in relation to different gelling agents, including organophilic montmorillonites, in the paint [28]. Although the sagging rate varies linearly with 1/(viscosity), as would be expected from a simple formula, the results also depend considerably on the gelling agent. It was suggested that the montmorillonite flakes are probably oriented parallel to the paint film and exert strong restrictive action on the flow.

The reinforcement of rubber with so-called hard clay was studied in relation to heat-treatment of the clay [26]. Generally the reinforcing ability is related to specific surface area of the clay, but the decrease in the reinforcement by heating above 500°C which produces little change in surface area suggests that the crystal structure of the mineral also has a significant role. The conclusion was drawn that the reinforcing effect results from the strong chemical activity of $(OH)^-$ ions on the lateral surface of the kaolinite.

A description was given of the synthesis of a trioctahedral magnesian silicate resembling hectorite and its gelling properties, after saturation with various octadecylammonium cations, in xylene and in mineral spirit [29]. Some of these preparations were found to have superior gelling properties to conventional organo-bentonite complexes.

*Papers presented included:*

1. *Clay-organic studies in the U.S.A.—A review.* G. W. Brindley.
2. *Clay-organic studies in Japan—A review.* E. Suito.
3. *Reactions between clays and organic compounds.* M. M. Mortland.
4. *Imogolite—organic interactions.* K. Wada, T. Inoue, and T. Henmi.
5. *Reaction of montmorillonite with acrylonitrile.* S. Yamanaka, F. Kanamaru and M. Koizumi.
6. *Surface activity and adsorption on kaolinite.* R. F. Conley.
7. *Trimethylsilation of calcium silicates.* I. Shiihara, K. Komatsu and I. Toyama.
8. *Physico-chemical methods.* H. van Olphan.
9. *Structural study of clay-organic complexes.* G. W. Brindley.
10. *Single crystal study of clay-organic complexes.* F. Kanamaru, S. Yamanaka and M. Koizumi.
11. *Interstratified structure of organo-montmorillonites revealed by electron microscopy.* E. Suito and T. Yoshida.
12. *Oriented adsorption of organic molecules as epitaxial nuclei.* N. Uyeda, M. Ashida, K. Yamamoto, T. Kobayashi and E. Suito.
13. *General aspects of the diffraction approaches to the problems.* M. Nakahira.
14. *Structure of alkyl-ammonium layer silicate complexes.* W. D. Johns.
15. *Kink formation in alkyl chains in montmorillonite.* A. Weiss.
16. *Thermal methods and techniques.* W. H. Slabaugh.
17. *Application of electron-probe microanalyser to clay studies.* R. Hayami.
18. *Cellular processes at work in sediments.* E. T. Degens.
19. *Role of clay mineral catalysis in genesis of petroleum hydrocarbons.* W. D. Johns.
20. *Explosiveness of benzoylperoxide mixed with bentonite.* D. Yamamoto.
21. *Surface and colloidal properties of clay-organic complexes.* H. van Olphen.
22. *Relations between surface modifying and surface properties of some kaolin minerals.* H. Takahashi and K. Tsutsumi.
23. *Spectroscopic methods in the study of clay-organic complexes.* M. M. Mortland.
24. *Applications of clay-organic complexes.* H. van Olphen.
25. *Industrial appiications of clay-organic complexes.* C. Kato.
26. *Reinforcement of rubber with hard clay.* M. Arakawa and E. Suito.
27. *Applications of clay-organic complexes.* W. H. Slabaugh.
28. *Rheological applications of organophilic montmorillonites.* H. Hasegawa and M. Kondo.
29. *Organophilic properties of synthetic trioctahedral montmorillonite-organic complexes.* M. Kondo and Y. Okamoto.
30. *Grinding of intercalated dickite and kaolinite.* S. Okuda and K. Inoue.
31. *The use of a differential refractometer.* G. W. Brindley.
32. *Summary of the seminar.* G. W. Brindley.

A small number of paper-bound copies of the Abstracts of Papers given at the Seminar on Clay-Organic Complexes (typewritten, 124pp.) can be obtained from Dr. M. Koizumi at the cost of postage by sea mail ($2) or by air mail ($5) per copy.

G. W. BRINDLEY (*U.S. Coordinator*)

*Materials Research Laboratory, and Department of Geosciences, The Pennsylvania State University, University Park, Pa. 16802, U.S.A.*

EIJI SUITO (*Japan Coordinator*)

*Institute of Chemical Research Kyoto University, Uji, Kyoto-fu 611 Japan*

M. KOIZUMI (*Seminar Secretary*)

*Institute of Scientific and Industrial Research Yamadakami, Suita, Osaka 565 Japan*

https://doi.org/10.1346/CCMN.1972.0200312 Published online by Cambridge University Press