

---

# Montmorillonite Complexes with Dioxane, Morpholine, and Piperidine: Mechanisms of Formation\*

G. W. Brindley and Atsumu Tsunashima

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

\*Clay-Organic Studies, XX.

**Abstract:** The absorption of dioxane, morpholine and piperidine from dilute aqueous solutions by Li-, Ca-, and Cu-montmorillonite is measured by means of a differential refractometer. This instrument measures small differences in the refractive indices of two liquids and provides a useful method for determining the amount of organic material removed from solution by the clay. Corrections are required for the effect of desorbed cations on the differential refraction measurements. Neutral molecules are absorbed in amounts related to the exchange capacity of the clay probably by cation-dipole interactions. The results are consistent with the formation of complexes  $\text{Li}^+-R$  and  $R-\text{Ca}^{2+}-R$  for the three organic materials used;  $\text{Cu}^{2+}$  ions behave like  $\text{Ca}^{2+}$  ions for dioxane, but form  $R-\text{Cu}^{2+}-RR$  complexes with morpholine and piperidine. Under acid conditions, morpholine and piperidine form organic cations  $\text{RH}^+$  which take part in cation exchange reactions and which are dominant at pH below about 5. Neutral molecule absorption also occurs by virtue of the presence of  $\text{RH}^+$  ions on the clay which form  $\text{RH}^+-R$  complexes (hemi-salt formation). When this last mechanism of absorption occurs, the total absorption is approximately twice that when a cation-dipole reaction or cation exchange alone operates. One-dimensional Fourier  $00l$  syntheses of complexes in equilibrium with aqueous organic solutions indicate that water molecules are associated with the clay-organic complexes to the extent of about  $5\text{H}_2\text{O}/\text{unit cell}$ .

*Clays and Clay Minerals*; August 1972 v. 20; no. 4; p. 233-240; DOI: [10.1346/CCMN.1972.0200408](https://doi.org/10.1346/CCMN.1972.0200408)

© 1972, The Clay Minerals Society

Clay Minerals Society ([www.clays.org](http://www.clays.org))

---