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Formation of a Clay Monolayer at an Air–Water Interface

Keiichi Inukai,[a] Yuji Hotta,[b] Masahiro Taniguchi,[b] Shinji Tomura[a] and Akihiko Yamagishi*[b]

[a] *National Industrial Research of Nagoya, Nagoya 462, Japan*
[b] *Department of Polymer Science, College of Science, Hokkaido University, Sapporo 060, Japan*

By measuring the surface pressure–area isotherm at an air–water interface, an ion-exchange adduct of synthetic saponite with trimethylstearylammonium cation has been revealed to form a monolayer which is transferred on a hydrophobic glass plate as an oriented multilayer film.

A clay is known to form an oriented film when its aqueous dispersion is cast on a solid surface.[1] Polarized spectroscopies have confirmed that clay particles are stacked with their silicate sheets in parallel with the film surface.[2] No reports of any attempt, however, to form an oriented clay film by transferring a monolayer from an air–water interface onto a solid substrate like a Langmuir–Blodgett film have been made.[3] If the method is applicable, it would be possible to prepare a clay film whose thickness is controlled on a molecular scale. The present work reports an initial attempt to form a clay monolayer at an air–water interface in order to prepare a multilayer clay film of uniform thickness.

Synthetic saponite (Smecton, Kunimine Ind. Co., Japan) was used as a clay sample, the cation exchange capacity (CEC) of which was 80 mequiv. per 100 g. In order to disperse the clay in chloroform, it was ion-exchanged with trimethylstearylammonium chloride, $NMe_3(C_{18}H_{37})Cl$. The ion-exchange adduct was prepared by mixing the clay with 2 equiv. of $NMe_3(C_{18}H_{37})Cl$ in water. After centrifugation, the precipitate was freeze-dried for 4 d; 10.0 mg of the adduct thus prepared was dispersed in chloroform (100 ml), resulting in a transparent suspension. The surface pressure–area isotherm was recorded at 25 °C with a Langmuir trough (a Monolayer Coating Unit, Joyce–Loebl).

Curves (*a*)–(*e*) in Fig. 1 are the pressure–area isotherms when 1–5 ml of the chloroform suspension was spread on pure water. In the case of curve (*b*) (V = 2 ml), for example, the surface pressure (π) rises from zero at an area of 480 cm^2 (denoted by A_1) and increases slowly upon decreasing the area to *ca.* 180 cm^2 (denoted by A_2). Beyond this point, π increases steeply to the measurable maximum surface pressure (55 mN m^{-1}). Virtually the same curves are obtained when the measurements are repeated after the surface is expanded to the initial area. Measured area A_1 (open circles) is plotted as a function of V in the inset of Fig. 1.

The chemical formula of the ion-exchange adduct was found to be $[NMe_3(C_{18}H_{37})]_{0.77}[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]$, giving a formula mass of 998. The surface area of a silicate sheet in a saponite unit cell is $a \times b$, *i.e.* 5.3 × 9.2 Å.[5] Assuming that a clay microcrystallite orients its silicate surface in parallel with the air–water interface, the total area covered by a clay monolayer A_m can be expressed as a function of V, eqn. (1), and is shown as a dotted line (x) in the inset of the figure.

$$A_m = 294\ V\ (\text{cm}^2) \qquad (1)$$

In a similar way, the theoretical area occupied by a bimolecular layer A_b is given by eqn. (2) which is indicated by a dotted line (y).

$$A_b = 147\ V\ (\text{cm}^2) \qquad (2)$$

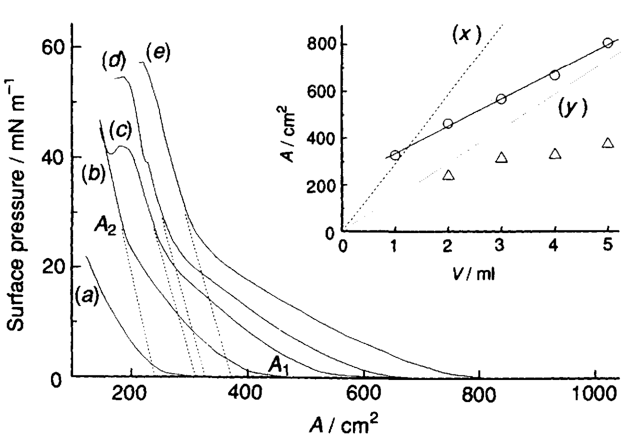

Fig. 1 Surface pressure–area isotherms when a volume (V) of a chloroform dispersion of a clay adduct (10 mg/100 ml) is spread on pure water: V = 1 (*a*), 2 (*b*), 3 (*c*), 4 (*d*) and 5 ml (*e*). Open circles and triangles in the inset represent values A_1 and limiting surface area as a function of V, respectively.

Comparing the experimental results with the theoretical predictions, the observed plot for A_1 falls between lines (x) and (y). Considering the ambiguity in estimating the surface of a clay crystallite, we conclude that the clay forms a monolayer at an air–water interface, at least in the region of $V \leqslant 2$ ml.

Based on the above model, the region between A_1 and A_2 may correspond to the process in which the surface density of clay particles increases, resulting in an increase of repulsive force. The surface pressure increases steeply beyond the area indicated by A_2. When the linear portion of the isotherm above A_2 is extrapolated to zero surface pressure, the limiting area is obtained, and its dependence upon V is represented by open triangles in the inset of Fig. 1. It is seen that the plot of the limiting area is a little below that expected theoretically for a bimolecular layer. Based on the results, we propose a mechanism in which the clay particles reduce their area in the region between A_1 and A_2 by increasing the fraction of a double-layer with the concomitant decrease of the monolayer region. At A_2, the whole layer is composed of a double layer. The formation of a multilayer thicker than a triple layer is assumed to be difficult.

A layer curve (*b*) can be transferred on a hydrophobic glass plate at π = 25 mN m^{-1} to form a 50-layer film. From X-ray diffraction measurements, the interlayer distance is determined to be 19.7 Å. Only (001) diffraction peaks are observed, confirming that the layers lie in parallel with the film surface.

The present work may open a way to the preparation of oriented clay films of uniform thickness on a molecular scale. Such films can be of value as surface modifiers in *e.g.* clay-modified electrodes.

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