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# Adsorption on hydrophobized surfaces: Clusters and self-organization

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### Abstract

The arrangement of liquid molecules on surfaces bristling with alkyl chains is deduced from adsorption studies, X-ray powder diffraction data, and microcalorimetric measurements of swelling-type layered materials, especially clay minerals. Small polar molecules such as water, ethanol, formamide, dimethylsulfoxide, and aromatic compounds are clustered between the alkyl chains pointing away from the surface. The energetic contribution related to the movement of the alkyl chains from direct contact with the surface atoms into upright positions is decisive. The importance of the interactions between the liquid molecules on the structure of the adsorption layer is clearly indicated by the changes of the adsorption layer thickness by salt addition. Thermodynamic data are obtained from surface excess adsorption isotherms from binary liquid mixtures combined with microcalorimetric measurements. Long-chain adsorptives such as long-chain alcohols interact with the surface alkyl chains by forming stable bimolecular films. These films undergo a series of higher-order phase transitions into kink- and gauche-block structures as the consequence of rotational isomerization of the alkyl chains. Such transitions are considered elementary processes in self-assembling films (layer-by-layer deposition, fuzzy films, Langmuir–Blodgett technique), and lipid membranes. © 2005 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Clay minerals; Hydrophobization; Kinks; Layered compounds; Self-assembling

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## 1. Introduction

Hydrophobization by long-chain compounds plays an important role in industrial applications. One example is the

flotation process [1]. The surfaces can be made hydrophobic by adsorption of long-chain compounds or grafting, i.e. formation of covalent bonds between the organic molecules and surface groups.

The hydrophobic character of a surface bristling with long alkyl chains seems to result from a complex interplay between the structure of liquid water and the interactions of the water molecules with the surface and the alkyl chain [2– 6]. In consequence, the degree of hydrophobization not only

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depends on the length of the alkyl chains and their distance [7] but also on their conformation. The conformation of the alkyl chains must be considered because conformational changes allow the chains to fit the assemblages of water molecules near the surface.

Intracrystalline reactive layered compounds [8–10] are excellent models for studying the arrangement and conformation of alkyl chains on surfaces and their interaction with liquid molecules. The surface of these compounds becomes hydrophobic when the interlayer cations are exchanged by long-chain organic cations, mainly alkylammonium ions. These cations remain attached to the surface by their cationic groups and are not displaced when the samples are dispersed in water or organic liquids. The liquid molecules are not only adsorbed at the external surface but also on the internal surfaces. The distance between the layers which is easily measured by X-ray powder diffraction gives information on the structure of the adsorption layer.

The most important group of intracrystalline reactive layer compounds are the three-layer (or 2:1) clay minerals [11–13]. Examples of other layered materials containing exchangeable cations are alkali layer silicates like kanemite and magadiite [14], molybdates, niobates, titanates, uranium micas, and M(IV) phosphates and arsenates [8–10]. Only one group of compounds, the layered double hydroxides, contains anions between the positively charged layers [15–17].

The advantage of clay minerals is that the density of the negative charges and therefore the packing density of the alkyl chains covers a broad range, increasing from smectites to vermiculites and micas (Table 1). The arrangement, orientation, and conformation of the long-chain compounds on the surface can be studied as a function of their packing density. When dispersed in liquids, the adsorption of the liquid molecules on and between the surface alkyl chains leads to different types of structures. Liquids consisting of smaller polar molecules like water, ethanol, N-methylformamide, dimethylsulfoxide tend to form clusters between the alkyl chains whereas polar long-chain compounds (nalkanols, n-alkylamines) due to their pronounced selfassembling behavior lead to well ordered bimolecular films between the host layers. In all cases the conformation of the alkyl chains often deviating from all-trans plays an important role. This interplay between liquid structure and conformation of the alkyl chains appears to be of importance in the actual studies of self-assembling systems



Fig. 1. Arrangement of primary *n*-alkylammonium ions in the interlayer space of swelling-type layer compounds as a function of the alkyl chain packing density (derived from the arrangement in the alkylammonium clay minerals).

and can be evaluated from studying the alkylammonium derivatives of swelling-type layer compounds.

#### 2. Alkylammonium ions on solid surfaces

Layered materials are easily hydrophobized by exchanging the inorganic cations on the external and internal surfaces by alkylammonium ions. The cation exchange is performed by dispersing the host materials in solutions of the alkylammonium chlorides or bromides [18]. During this reaction the interlayer space takes up the alkylammonium ions as counterions, water molecules, and some further alkylammonium ions together with chloride or bromide forming ion pairs. The basal spacings are therefore relatively high (>2 nm) and depend on the amount of intercalated ion pairs and water [19–22]. After washing and drying (usually at ~65 °C in vacuum), a clear relationship exists between the chain length of the alkylammonium ions and the basal spacing which expresses the different arrangements of the alkyl chains (Fig. 1) [18].

Short chain alkylammonium ions are lying flat on the surface in a monolayer, the so-called h1 structure (Fig. 2). Alkylammonium ions which are too long to be packed in monolayers form bilayers (h2 structure). The critical chain length at the monolayer/bilayer transition is related to the layer charge density and provides the best

Table 1

Clay mineral data: lattice dimensions a, b; layer charge  $\xi$ , surface charge density  $\sigma_{\alpha}^{a}$  and equivalent area (area per charge)  $A_{e}$ 

Mineral	Origin	<i>a</i> (nm)	b (nm)	$\xi$ (eq/unit)	$\sigma_{\rm o}~({\rm Cm}^{-2})$	$A_{\rm e} ({\rm nm}^2)$
Vermiculite	South Africa	0.535	0.925	0.75	0.25	0.33
Beidellite	Rhön, Germany	0.518	0.900	0.42	0.15	0.55
Montmorillonite	Wyoming	0.518	0.900	0.28	0.10	0.83
	Bavaria			0.28	0.10	0.83

<sup>a</sup> Surface charge density  $\sigma_0 = 1.62 \times 10^{-19} \xi/ab$  (Cm<sup>-2</sup>).

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