

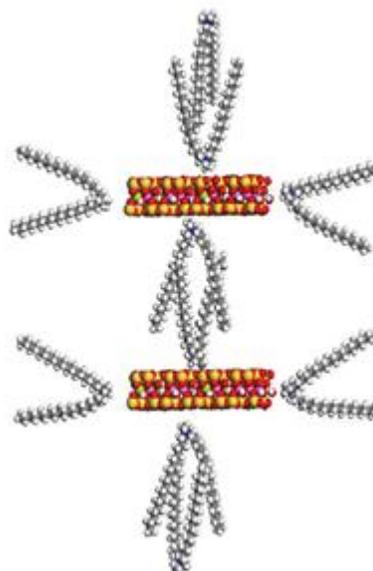
Nature of the interlayer environment in an organoclay optimized for the sequestration of dibenzo-p-dioxin

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Abstract

A Na-smectite clay (Na-SWy-2) was exchanged with various amounts of dimethyldioctadecylammonium bromide (DODA-Br) up to twice the cation exchange capacity (CEC). The organoclay (DODA-SWy-2) with DODA-Br added at 2xCEC exhibited a maximum 4.2 nm d-spacing and a 31.4% carbon content, which demonstrates DODA⁺ intercalation. DODA-SWy-2 was evaluated as an archetype of commercial products used to sequester hydrophobic contaminants and the nature of the primarily C18 alkylhydrocarbon- chain interlayer environment was emphasized. Shifts in $\nu(\text{CH})$ and CH_2 rocking band positions in DODA-SWy-2-complex FTIR-spectra indicate that DODA C18 chains were more ordered as DODA surface coverage was increased. Differential scanning calorimetry analysis indicated a DODA-SWy-2 gel-to-liquid transition temperature much lower than crystalline DODA-Br and similar to aqueous DODA-Br vesicles. This suggests that the transition was governed by C18 alkyl tail-tail interactions in the clay interlamellar region. Dibenzo-p-dioxin (DD) sorption from water by DODA-SWy-2 was compared to DD sorption by the geosorbents, granular activated carbon (GAC), K-exchanged saponite, and a muck soil. The Log K_f values from a fit of the sorption isotherms to the Freundlich model were 4.36 for DODASWy-2, 5.44 for GAC, 3.11 for muck soil, and 2.39 for K-saponite. The DD-organic-matter-normalized sorption coefficient (K_{om}) was ~2.5 times the octanol-water partition coefficient (K_{ow}). This indicates that DD has a higher affinity for the nonpolar interlayer DODA organic phase than for octanol. In contrast, the K_{om} for muck soil DD sorption was ~10 times less than K_{ow}, which reflects the higher polarity of amorphous soil organic matter relative to octanol. Enhanced DD uptake by the DODA-derived lipophilic phase in the organoclay is attributed to the low polarity, 'open' C18 alkyl structure due to the physical dimensions of 'v-shaped' DODA⁺ molecular, and low density of the interlamellar phase (~0.50 g/cm³) density of intercalated DODA⁺.



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