
Mobility of Small Molecules in Interlayers of Hectorite Gels: ESR Study with an Uncharged Spin Probe

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Abstract: Electron spin resonance (ESR) spectroscopy was used to measure the rotational mobility of an uncharged nitroxide spin probe (4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy) in hectorite gels of variable water content. Physical adsorption segregated the probe molecules into two populations: probes in the solution or a solution-like phase, and motionally restricted probes in the adsorbed phase. Although the spectra of these two populations were discrete, indicating that exchange between them was slow on the time scale relevant to ESR, their overlap prevented a straightforward determination of mobility of the adsorbed probes. Even though adsorption was weak, effects of the adsorbed population on the spectral lineshape were detectable for suspensions containing as little as 20 grams clay per liter of water. Orientation of the adsorbed probes on the fully hydrated hectorite surfaces was similar to that of a positively charged nitroxide probe, suggesting that steric factors rather than electrostatic forces control short-range organic molecule interaction with the silicate. The possibility of reaching false conclusions about probe mobility and interlamellar water viscosity when using a weakly adsorbing probe is discussed.

Key Words: ESR • Hectorite • Molecular mobility

Clays and Clay Minerals; August 1994 v. 42; no. 4; p. 455-461; DOI: [10.1346/CCMN.1994.0420412](https://doi.org/10.1346/CCMN.1994.0420412)
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