s N_2 at low relative pressures (*P*/*P*⁰). By contrast, EGME shows higher uptakes than N_2 on all exchanged clays at all *P*/*P*⁰. The anomaly for water is attributed to its relatively low attraction for siloxane surfaces of montmorillonite because of its high cohesive energy density. In addition to solvating cations and expanding interlayers, water and EGME vapors condense into small clay pores and interlayer voids created by interlayer expansion. The initial (dry) interlayer separation varies more significantly with cation type than with layer charge; the water-saturated interlayer separation varies more with cation type than the EGME-saturated interlayer separation. Because of the differences in surface adsorption and interlayer expansion for water and EGME, no general correspondence is found between the isotherms of water and EGME on exchanged clays, nor is a simple relation observed between the overall uptake of either vapor and the cation solvating power. The excess interlayer capacities of water and of EGME that result from lattice expansion of the exchanged clays are estimated by correcting for amounts of vapor adsorption on planar clay surfaces and of vapor condensation into intrinsic clay pores. The resulting data follow more closely the relative solvating powers of the exchanged cations.

Key Words: Cation Solvation • EGME Isotherms • Excess Interlayer Uptake • Exchanged Cation • Interlayer Spacings • Layer Charge • Layer Separation • Microporosity • Montmorillonite • Surface Adsorption • Water Isotherms

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