The Cs/K Exchange in Muscovite Interlayers: An Ab Initio Treatment

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Abstract: Plane-wave pseudopotential total energy calculations have been applied to investigate the structure and energetics of the Cs/K exchange into interlayer sites in muscovite mica. Novel muscovite structures were designed to isolate the effects of 2:1 layer charge, cation size/interlayer site shape, and tetrahedral Al/Si substitutions on the exchange. All atom and cell-parameter optimizations were performed with the intention to mimic the constant pressure, non-isovolumetric exchange conditions thought to be found at frayed-edge sites. Under conditions where the cell parameters are allowed to relax, the overall Cs/K exchange reaction is surprisingly close to isoenergetic. The forward reaction is more strongly favored with increasing layer charge. For the condition of zero layer charge and no interlayer site distortion, the difference in the optimal interlayer spacing for Cs relative to K is very small, indicating a baseline indifference of the muscovite structure to cation size. The presence of 2:1 layer charge or tetrahedral rotations arising from Al/Si substitutions clearly change this outcome. Analysis of the dependence of the interlayer spacing on layer charge shows that while the spacing collapses with increasing layer charge for K as the interlayer cation, the reverse is true for Cs. We attribute the contrasting behavior to inherent differences in the ability of these cations to screen 2:1 layer-layer repulsions. Such effects might be involved during exchange at frayed-edge sites where interlayer spacings are increased. This is known, from experiment, to be very selective for Cs. Overall, the exchange energetics are so low that the Cs/K exchange rate and degree of irreversibility are likely to be dominated by diffusion kinetics.

Key Words: *Ab Initio* • Cation Exchange • Cesium • Clay • Defects • Density Functional Theory • Exchange Energy • Isomorphic Substitution • Mica • Muscovite

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