"Modeling Impact of Intermolecular Interactions of LPG—Alcohol Mixtures on Stability of Phyllosilicates: Towards Improvement of Drilling Fluids"

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Liquefied petroleum gas (LPG) mixtures have shown potential as more viable drilling fluids (DF) in the process of shale fracturing, better known as fracking, as opposed to currently used water-based DFs. LPG-based DFs are, conceptually, a more appropriate option, since they preserve the integrity of the shale minerals' structures, which often deteriorates, therefore causing borehole failures. LPGs stabilize shale minerals by achieving a balance between the polar and non-polar interactions found among the organic components of the LPG DFs and the phyllosilicates – unit cell networks of the shale minerals.

Propane and butane are primary components of LPGs. Polyhydric alcohols (ethylene glycol, glycerol) have shown potential as effective additives for LPGs. Therefore, these organic molecules have been chosen for the current project. To ensure feasibility of the computations, a phyllosilicate model was selected (Figure 1a). The structure was initially obtained from empirical crystallization studies and further optimized with quantum chemistry methods. Taking into account that most interactions of the shale mineral with DF occurs at defects (cracks, edges and open surfaces of phyllosilicate), and the contact surface of a single LPG component molecule under study with phyllosilicate is small, the chosen structure satisfies those modeling requirements. The first phase in examining LPG–phyllosilicate interactions involved optimization of a phyllosilicate model, as well as single propane, butane molecule, ethylene glycol or glycerol molecules followed by modeling of LPG component – phyllosilicate complexes (Figure 1). In addition, modeling of phyllosilicate – water interactions has been performed, to compare to LPG.
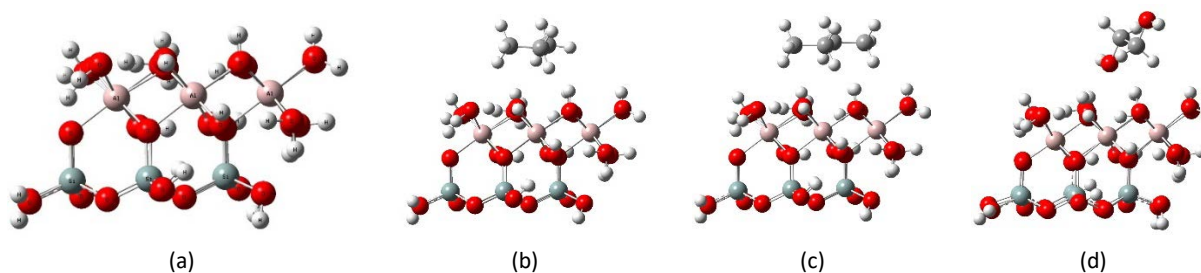

| (a) | (b) | (c) | (d) |

Figure 1. Optimized structure of the phyllosilicate model (a) and phyllosilicate complexes with an LPG component: propane (b), butane (c), ethylene glycol (d). Only top (aluminum oxide side) binding is shown here. See Figure 2 for further details regarding orientation.

Both the phyllosilicate and LPG components were optimized at the M05-2X/6-31G(d, p) level of theory with Grimme's empirical dispersion correction. Constrains have been imposed on the Al, Si and O atoms of the phyllosilicate structure to ensure the crystal model stays intact. Unsaturated oxygen atoms at the faces/edges of the phyllosilicate model have been capped with hydrogen to compensate excessive negative charge. Each LPG component/phyllosilicate system was optimized in six different orientations chosen relative to the corresponding distinctive phyllosilicate crystal faces (Figure 2).
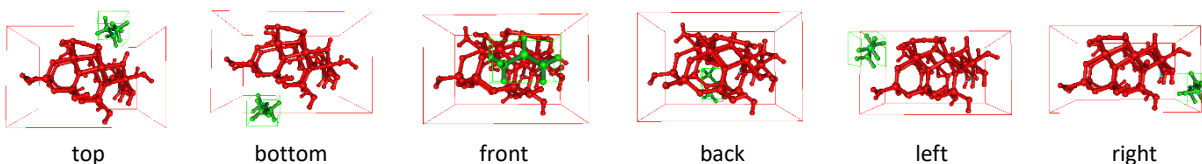

| top | bottom | front | back | left | right |

Figure 2. Orientation of LPG components with respect to each of the six distinctive faces of the phyllosilicate model. Color coding represents the fragments as assigned for PIEDA analysis: red – phyllosilicate, green – an LPG component (propane is pictured).

Following geometry optimization, the change in energy was calculated for comparison among the phyllosilicate, propane, ethylene glycol, glycerol and water molecules and the phyllosilicate-LPG component systems. The system having the highest energy gain typically indicated a stronger intermolecular interaction, and therefore, a more stable molecular structure. The most energetically favorable interaction faces of the crystal for each LPG were determined. The non-polar LPG components under study (propane and butane) displayed a preference for interaction with the flatter top and bottom faces of the phyllosilicate (Figure 2). The propane preferred the bottom orientation (the silica side) over every other facial plane with a calculated energy of binding -5.62 kcal/mol lower than the separated system. The butane preferred the top orientation (the aluminum side) over every other facial plane with a calculated energy of binding -7.84 kcal/mol. For each of these molecules the other planer facial side was the second lowest binding energy with a relative binding affinity <1 kcal/mol than the highest preferred plane. The other facial sides of the phyllosilicate, which theoretically represent cracks and other imperfections, display a much lower affinity for these two molecules. Calculations on the ethylene glycol/phyllosilicate system displayed a stronger affinity for the left facial orientation of the crystal (Figure 2). Water and glycerol computations are currently being finalized. The results of the preliminary optimization were largely in agreement with theoretical considerations. In contract, ethylene glycol strongly preferred the left side of the crystal, which in this experiment represents a crack, edge or imperfection in the crystal. Ethylene glycol is able to form hydrogen bonds and would form be most energetically favorable complex with the phyllosilicate. The planer surface is largely unable to form hydrogen bonds in this way. The edge offers ethylene glycol four hydrogen bonding sites, which allow a more satisfactory orientation for this molecule.

Each facial orientation of the phyllosilicate/LPG system was further analyzed using Fragment Molecular Orbital (FMO) quantum calculations in the GAMESS computation chemistry software. These calculations were performed using the 2nd order Møller–Plesset perturbation theory (MP2) with 6-31G(d, p) basis set. Pair Interaction Energy Decomposition Analysis (PIEDA) was performed on obtained phyllosilicate/LPG complexes in order to evaluate main components of the interaction energy that include: dispersion, exchange repulsion, electrostatic, and charge transfer (CT) terms. Table 1 displays the results for the propane/phyllosilicate complex.

Table 1. Pair interaction energy decomposition analysis of propane/phyllosilicate interaction energy (kcal/mol).

Crystal Face	Dispersion	Exchange Repulsion	Electrostatic	CT + High Order Terms	Total
top	-8.551	9.562	-4.348	-3.381	-6.72
bottom	-7.19	6.255	-3.325	-2.981	-7.24
left	-7.655	9.695	-5.519	-3.745	-7.22
right	-5.958	6.591	-4.258	-2.691	-6.32
front	-6.736	8.181	-6.725	-2.839	-8.12
back	-6.207	6.808	-3.094	-2.453	-4.95

The analysis of the energy terms for propane/phyllosilicate complex shows that dispersion contribution is the highest. The same trend has been observed for butane. In contrast, electrostatic affinity is the strongest in the ethylene glycol/phyllosilicate complex. These results reflect the predictions one would have made based on the structure of the LPG components under study.