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

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In this project we continue investigation of liquefied petroleum gas (LPG) mixtures as a base for drilling muds. Potential consequences of LPG-mixtures interactions with phyllosilicate complexes (Figure 1) are also investigated. As we previously reported polarity of LPG-containing mixtures is critical for intermolecular interaction of LPG mixtures with phyllosilicates. Over this reporting period, we continued assessment of LPG components and additives. Specifically, interactions between the phyllosilicate cluster and additional LPG-mixture components were analyzed. We considered propane, butane, and isobutene as LPG components and polar polyhydric alcohols as LPG additives. Ethylene glycol and glycerol are considered as LPG additives increasing the

Figure 1. Optimized structure of the phyllosilicate model

mixture polarity. Following the proposed methodology, interactions of LPG components with each face (top, bottom, right, left, front, and back) of the phyllosilicate cluster were analyzed (Figure 2). Additionally, a phyllosilicate-water system was considered as a reference (a strongly polar environment) for intermolecular interactions.
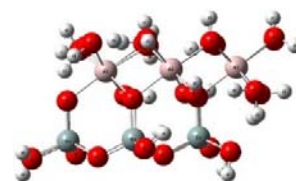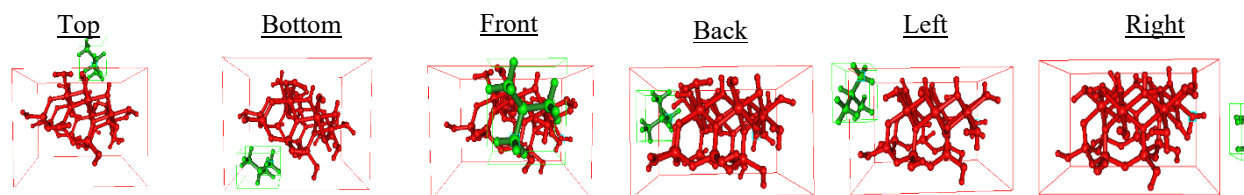
| Top | Bottom | Front | Back | Left | Right |

Figure 2. Interactions of isobutene (green) with the phyllosilicate model. Color coding represents PIEDA fragments.

The optimization of molecular complexes were performed at the M05-2X/6-31G** level of theory with the Grimme's empirical dispersion correction. The polarized continuum model (PCM) was used to represent solvents. Interaction energies in the molecular clusters were calculated with the Pair Interaction Energy Decomposition Analysis (PIEDA) based on the two-body approximation of the Fragment Molecular Orbital Method (FMO2) and using the 2nd order Møller–Plesset perturbation theory (MP2).

In addition to our previous findings (interactions in the propane-phyllosilicate complex), we have investigated interactions of isobutate and butane with the phyllosilicate cluster. In the presented (PIEDA) analysis the interaction energy is represented as a sum of the following terms: dispersion, solute-solvent, exchange-

Table 1. Pair interaction energy decomposition analysis (PIEDA) of isobutane - phyllosilicate interaction energy (kcal/mol).

Crystal Face	Dispersion	Exchange Repulsion	Electrostatic	CT + High Order Terms	Total
Back	-7.5	8.45	-6.03	-3.40	-8.47
Bottom	-8.37	7.26	-2.96	-3.59	-7.67
Front	-6.18	6.13	-2.37	-2.69	-5.11
Left	-7.8	8.85	-4.10	-3.56	-6.65
Right	-7.18	8.11	-4.47	-3.37	-6.91
Top	-7.74	8.24	-4.02	-2.82	-6.35

repulsion, electrostatic, and charge transfer (CT). Table 1 displays results for the isobutane-phyllosilicate complex as an example. 'Back' and 'bottom' conformations show the strongest (-8.47 and –7.67 kcal/mol respectively) total interaction energies. In this system, as one may expect, the main attractive contribution comes from the dispersion term and the electrostatic and charge transfer interactions are mainly compensated by the exchange-repulsion term. For all considered systems we obtained interaction energies and determined main PIEDA components. Also, we investigated relative energies of LPG additive-phyllosilicate clusters that are presented in Table 2. In particular, the results show that the 'back' conformation provides the lowest energy while the 'right' conformation leads to the highest energy (least optimal conformation) of the ethylene glycol-phyllosilicate complex. For glycerol, the 'left' conformation has the lowest energy and the 'bottom' conformation has the highest energy. On average, energies of

the glycerol-phyllosilicate complex are lower by around ~8.5 kcal/mol as comparted to the ethylene glycol-phyllosilicate complex.

Also, we have analyzed molecular geometries of LPG-phyllosilicate complexes (Table 3). Analysis of molecular geometries is based on measurements of distances and angles between the closest atoms of the phyllosilicate cluster and LPG components and additives. The analysis shows that, as expected, the shortest intermolecular distances corresponds to O…H-O interactions (hydrogen bonds) while the longest correspond to electrostatic interactions of C-H…O type.

The next phase of the project employs computational thermodynamics methods for calculations of Gibbs energies and chemical potentials of LPG mixtures and LPG-phyllosilicate complexes.

These methods are based on the COSMO-RS theory. The COSMO-RS is an extension of the traditional conductor like screening model (COSMO) of a solvent. This method utilizes an *ab initio* calculated σ-profile representing a charge density on a hypothetical surface (similar to the Van der Waals surface) surrounding a molecule or ion. The σ-profile is calculated for a given molecule of interest (e.g. an LPG component). For example, (Figure 3) σ-profile of a non-polar molecule (propane) has a narrow peak around zero (surface is mostly neutral), while polar molecules (ethylene glycol and water) have peaks that correspond to localization of positive and negative surface electric charges attracted by polar oxygen and hydrogen atoms. The σ-profile is used in statistical thermodynamics calculations to obtain chemical potentials of liquid mixtures or LPG- phyllosilicate complexes. COSMO-RS is currently used by our group to carry out calculations of solubilities, vapor-liquid, liquid-liquid phase diagrams, chemical potentials, and partition coefficients of LPG components and additives. The COSMO-RS method is implemented in the *COSMOTherm* software that has been purchased with funds provided by this grant.

This grant also provides opportunities for undergraduate students at Monmouth University for participation in the Summer Research Program where students learn basics of computational chemistry in a research lab setting. Also, this ACS-PRF grant is important for the PI's professional activates as it provides resources for development of novel computational methodologies that result in peer-reviewed publications and presentations at professional meetings. Grant covers summer stipends for undergraduate students and for the PI and provides travel funds for attending professional meetings.

Table 2. Relative energies of interactions of LPG additives with the phyllosilicate cluster.

Ethylene glycol		Glycerol	
Face	*E, kcal/mol*	*Face*	*E, kcal/mol*
Back	0.00	Back	2.93
bottom	16.03	bottom	9.39
front	14.34	front	2.20
left	12.58	left	0.00
right	23.18	right	8.68
top	3.29	top	1.28

Table 2. Example of geometrical parameters of intermolecular interactions between phyllosilicate cluster and considered molecules in the top orientation.

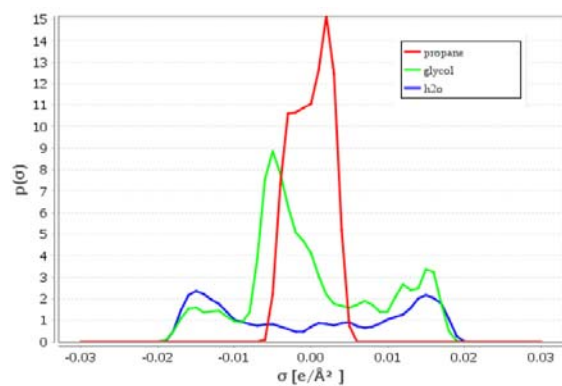| Molecule	Interaction	Angle, deg	Distance, Å
Propane	C-H…O	154.9	2.68
Butane	C-H…O	153.4	2.68
Ethylene Glycol	O…H-O	157.1	1.89
Water	O-H…O	150.9	1.76
Isobutane	C-H..O	168.1	2.56
Glycerol	O…H-O	153.2	1.95

Figure 3. COSMO-RS σ-profiles of propane (red), ethylene glycol (green), and water (blue) are shown.