Theoretical Investigation Of The Effect Of Cushion Gas On The H2/water Interface And H2 Underground Storage

S. Alshammari, M. Abu Alsaud, S. Ayirala, A. Yousef, Saudi Aramco PE&D

Abstract

Objectives/Scope: Underground H2 storage is a promising solution for storing H2 at a large scale in the subsurface. However, there are no studies reported in the literature that explains interfacial tension trends of H2/water when mixed with a cushion gas. The objectives of this paper are: (1) to investigate the effect of methane and carbon dioxide as cushion gases on the interfacial tension (IFT) of H2/DI water, and (2) to explain the observed IFT trend in terms of molecular interactions.

Methods, Procedures, Process: Molecular dynamics simulation of H2/H2O, H2-CH4/H2O, and H2-CO2/H2O systems were carried out at a constant temperature of 300 K and varying pressures (5 to 20 MPa) using GROMACS software package. Nonbonded dispersion interactions were cutoff at a distance of 1.2 nm and the electrostatic forces were treated with particle mesh Ewald summation. Energy minimization through the steepest decent algorithm was done followed by 100 ps of NVT equilibration and 50 ns NVT production run. The pressure was regulated through adjusting the number of gas molecules based on Peng Robinson equation of state. Quantum chemical calculations using the symmetry adapted perturbation theory (SAPT) were carried out for gas-H2O dimers using Psi4.

Results, Observations, Conclusions: Density profiles of the studied systems show that carbon dioxide adsorbs more strongly on the water surface compared to methane. Therefore, the decline in IFT is more pronounced for H2-CO2 compared to H2-CH4. Increasing the pressure did not affect the IFT for pure H2/H2O whereas adding CH4 or CO2 resulted in IFT drop at higher pressures. Carbon dioxide and hydrogen mixture has a much steeper IFT decline than that of methane and hydrogen. The molecular interactions energy between gaseous molecules and water was much higher for the CO2 mixture compared to that of CH4. The quantum chemical calculations showed the same trend for geometrically optimized dimers of H2, CH4, and CO2 with H2O. Electrostatic interaction energy was higher than polarization and dispersion for the carbon dioxide/water dimer while methane/water interactions via dispersion were more than those by electrostatic forces. Repulsive exchange interactions due to the Pauli exclusion principle had the same trend as the molecular size of the studied molecules. These results indicate that CO2 is effective in lowering the capillary pressure than CH4 as a cushion gas, which has direct implications to favorably affect the underground H2 storage.

Novel/Additive Information: This study uncovers the reason behind the observed IFT trends of hydrogen mixtures with methane and carbon dioxide through classical molecular dynamics simulation and quantum chemical calculations. In addition, it also sheds several novel insights about the impact of different cushion gases on underground H2 storage potential.