Molecular dynamics studies on shale gas and fracturing fluid diffusivity in shales

L. D. Peristeras[1*], K. D. Papavasileiou[1,2], I. G. Economou[1,3]

[1]National Center for Scientific Research "Demokritos", Institute of Nanoscience and Nanotechnology,
Molecular Thermodynamics and Modelling of Materials Laboratory,
Aghia Paraskevi Attikis, Greece
[2]Scienomics SARL, Paris, France
[3]Texas A&M University at Qatar, Chemical Engineering Program, Doha, Qatar
[*]l.peristeras@inn.demokritos.gr

The steady decline in conventional fuel resources as well as their environmental footprint has led to the question of efficient exploitation of unconventional hydrocarbon reservoirs. Shale gas, which is natural gas hosted in shale formations, has revolutionized the energy industry [1] and the global abundance of shale and mudrock formations has generated great hope in producing high quality transportation fuels, which lack aromatic hydrocarbons, generate lower emissions and can be directly used to cover industrial and consumer needs. Shale formations are chemically and structurally diverse, containing kerogen, clay, calcite and quartz, in analogies that vary substantially from region to region. Kerogen is a microporous amorphous solid and the major component of the organic matter scattered in the potentially lucrative shale formations hosting shale gas. A deeper understanding of the way kerogen porosity characteristics affect the transport properties of hosted gas is important for the optimal design of the extraction process [2]. To this end, we employed molecular dynamics (MD) simulations to investigate the role of porosity on the adsorption and transport behavior of shale gas in overmature type II kerogen found in many currently productive shales. The diffusion of CH_4, C_2H_6, and CO_2, both as pure components and as constituents of the quaternary mixture, was investigated at temperatures of 298.15 and 398.15 K and pressures of 1 and 250 atm. The diffusion was found to be anisotropic and the maximum component of the diffusion coefficient correlates linearly with the limiting pore diameter (LPD), indicating that the controlling step of the transport process is the crossing of the limiting pore region [3]. On the other hand, clay minerals are hydrous aluminosilicates, characterized by an extensive network of micropores and mesopores. Among them, kaolinite is one of the most abundant on Earth and is commonly encountered in shales. Fracturing fluids are mostly water-based and contain a number of chemicals in small volumes such as methanol and citric acid as well as elevated levels of Sr^{2+}, Na^{+} and Cl^{-} ions and naturally occurring radioactive materials (NORM) such as Ra^{2+} isotopes. Our MD simulations of model fracturing fluids in kaolinite slit pores at ambient temperature and pressure showed that confinement results in mobility reduction of all components compared to the bulk, with this reduction being especially pronounced near kaolinite's gibbsite surface due to extensive hydrogen bond formation. Citric acid has a more profound effect on mobility compared to methanol, since the formation of clusters hinders the motion of all fluid components [4]. Given the experimental difficulties in probing the relevant mechanisms at the aforementioned scale, our results are expected to assist in predicting the fate of fracturing fluids additives and contribute towards formulation and design of environmentally friendly fracturing fluids that limit the amount of NORM released from a shale without compromising the extraction process.

References

[1] A. Striolo, D. R. Cole: *Understanding shale gas: recent progress and remaining challenges.* Energy Fuel **31**, 10300-10310 (2017).
[2] M. Vasileiadis, L. D. Peristeras, K. D. Papavasileiou, I. G. Economou: *Modeling of bulk kerogen porosity: Methods for control and characterization.* Energy Fuels **31**, 6004-6018 (2017).
[3] M. Vasileiadis, L. D. Peristeras, K. D. Papavasileiou, I. G. Economou: *Transport properties of shale gas in relation to kerogen porosity*. J. Phys. Chem. C **122**, 6166-6177 (2018).
[4] K. D. Papavasileiou, V. K. Michalis, L. D. Peristeras, M. Vasileiadis, A. Striolo, I. G. Economou: *Molecular dynamics simulation of water-based fracturing fluids in kaolinite slit pores*, J. Phys. Chem. C **122**, 17170-17183 (2018).