Fast calculation of solvation structure and thermodynamics in supercritical CO_2

CAROF Antoine[a]; HOUSSEIN MOHAMED Mohamed[a]; INGROSSO Francesca[a;]
BORGIS Daniel[b]; BELLONI Luc[b]

[a]LPCT, Université de Lorraine, CNRS, Nancy 54000;

[b]PASTEUR, Département de Chimie, Ecole Normale Supérieure, PSL University, Sorbonne Université, CNRS, Paris 75005, France

[c] LIONS, NIMBE, CEA, CNRS, Université Paris-Saclay, Gif-sur-Yvette 91191, France

antoine.carof@univ-lorraine.fr

Growing concern about the environmental impact of industrial activities is driving the chemists to develop more ecological processes. A major goal is to design new range of solvents, “greener” but as efficient as the widely used organic solvents. Supercritical CO_2 ($scCO_2$) is an interesting alternative.[1] It is non-toxic to humans and the environment, non-flammable and can be easily fine-tuned to precisely control the solvation power. The $scCO_2$ is used in several industrial processes: extraction of natural products, impregnation of polymer matrices, water purification or synthesis of nanoparticle A wider use of such ecological solvent would however require an accurate for predicting the solvation properties.

Different approaches exist to estimate the solvation properties in supercritical fluids. Industrial chemists rely on accurate parametric models, but many parameters must be fitted for each solute and each new solvent.[2] Molecular simulations (MD or DFT) are more flexible than the parametric models and can accurately calculate the solvation free energy and the other solvation properties: structure, enthalpy, molar volume. But despite enormous progress, MD is still too expensive to be considered as a predictive tool for large scale investigations (many solutes, different solvents and solvent mixtures and different thermodynamic conditions).[2]

We will present a powerful alternative strategy based on classical density functional theory (cDFT), a liquid-state theory. Such approaches provide the same solvation properties as MD, but at a computational cost that is 1000 times cheaper.[3] In our work, we built the excess free energy functional and compared the structure and the solvation free energy of several solutes in $scCO_2$ obtained with cDFT and MD.[4] We obain a very good agreement between MD and cDFT In this talk, we will detail the method, the implementation and the perspective for the development of this new accurate, flexible, and ultrafast prediction tool for solvation properties in $scCO_2$.

References

[1] C. Song, Catal. Today (2006) **115,** 2-32.
[2] L.F. Vega, J. Supercritical Fluids (2018) **134**, 41-50.
[3] L. Ding, M. Levesque, D. Borgis, L. Belloni, J. Chem. Phys. 2017) **147**, 094107.
[4] M. Houssein Mohamed, L. Belloni, D. Borgis, F. Ingrosso, A. Carof, arXiv:2310.14667 (2023).