June 7, 2023

Reviewer's Report on Meysam Aryafard's Thesis

Biomolecular interactions at the surfaces in aqueous and non-aqueous solutions

The thesis presents a combined experimental and molecular-level study dealing with deep eutectic solvents (DESs), ionic liquids (ILs) and their binary mixtures as green solvents, including demonstration of their solvent capabilities. In particular, the author on one hand synthesised new ILs and DESs and on the other hand also carried out molecular dynamics (MD) simulations of DES-IL systems to provide insights into their microstructure. This makes outcomes of the thesis rather valuable. The results of the thesis were published in six peer-reviewed papers; in four papers, Meysam Aryafard is the first author. This provides evidence about importance and quality of author's contributions to the field, and it makes my reviewing task easier.

The thesis is written using a journal style, i.e., as a "guide"/comments to author's papers which are included in Appendices. The thesis is written in cumbersome english. Theoretical sections of the thesis after an introductory chapter is divided into two logical parts and they prepare ground for presentation of the experimental and modelling results. The first part provides theoretical background of solvents with emphasise on DESs and ILs. The second part summarises MD simulation technique employed. The solvent section describes adequately the polarity of solvents, solvatochromic properties, and preferential solvation (PS) model in relation with DESs and ILs. The MD section is too general, contains unnecessary text book details and would require improvements. For example, the author presents equations of motion for the microcanonical ensemble while actual MD simulations were carried out in canonical or isothermal-isobaric ensembles, i.e., the MD section should also cover thermostats and barostats. Also the author did not mention or discuss choice of force field parameters and determination of partial charges for DESs, ILs, co-solvents or solutes. E.g., is consensus about the most adequate force field(s) for DESs or ILs? This is crucial for faithful modelling of interactions of complex DES/IL/co-solvent/solute systems.

On one hand, result sections of the thesis demonstrate rather impressive amount of experimental and modelling effort and results accomplished by the author. On the other hand, the result sections are not easy to follow and they are rather descriptive. It would help to summarise motivation and goals for systems studied at the beginning of the result sections. First, the author focused on the interactions in complex DES/IL/co-solvent systems using targeted experiments and MD modelling complemented by DFT calculations. The results are primarily presented and discussed in terms of the radial distribution functions (RDFs) and determined parameters for the PS model. It should be noted that the spatial distribution functions (SDFs) may provide better characterisation of solvation structures than RDFs. Nevertheless, obtained results seem to provide valuable molecular-level insights into these complex systems. This is followed by MD

Research Group of Molecular and Mesoscopic Modelling
Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Rozvojova 135, 165 02 Praha 6, Czech Republic
www.icpf.cas.cz | Tel: +420 220 390 111 | Fax: +420 220 920 661 | iccas@icpf.cas.cz

simulations of biochar in aqueous solutions and its sorption for tetracycline as a water pollutant, and synthesis of a series of novel protic ionic liquids and low melting mixtures. Finally, the author studied use of ILs for cellulose dissolution. Although, the use of ILs as solvent for dissolution of cellulose is not a new or novel approach author's MD simulations on IL-cellulose systems contributed to our understanding of mechanism of cellulose dissolution.

After thoroughly reading the thesis and despite my criticism, I recommend the thesis for defence.

prof. Ing. Martin Lísal, DSc.

Research Group of Molecular and Mesoscopic Modelling
Institute of Chemical Process Fundamentals of the CAS, v. v. i.
Rozvojova 135, 165 02 Praha 6, Czech Republic
www.icpf.cas.cz | Tel: +420 220 390 111 | Fax: +420 220 920 661 | iccas@icpf.cas.cz