OPPONENT'S REPORT
ON
MEYSAM ARYAFARD'S DOCTORAL DISSERTATION
ENTITLED
"BIOMOLECULAR INTERACTIONS AT THE SURFACES IN AQUEOUS AND NONAQUEOUS SOLUTIONS"

The thesis is based on 6 scientific papers published in highly reputable international journals. Consequently, there is no doubt that the candidate has a sufficient number of publications to fulfill the requirements of the doctoral school for obtaining a PhD. However, to my understanding of my role in the PhD procedure, I must evaluate the thesis which is in stark contrast to the published papers.

Overall, the quality of English in the PhD thesis is rather poor, leading to the utilization of overly general statements and a low information density in the text. Reading the text becomes unpleasant due to the sentences without meaning, the lack of cohesion among the sentences and no aiming to tell a cohesive story through the thesis.

I believe the PhD candidate is capable for that since the thesis includes appealing figures which requires high involvement of its creator. Therefore, I recommend the PhD candidate, if intending to pursue a career in science, he should dedicate more effort to improving the quality of their written English and pays closer attention to the presentation quality of his work.

For instance, I find it quite frustrating how little added value there is in the annotation (page iv) and in the Introduction. It is unusual to come across a PhD thesis introduction that lacks any cited references and is as brief as half a page. I was also a bit surprised that there is no summary/abstract in the thesis at all.

According to the title, Chapter 2 is intended to cover the topics of solvent polarity and the solvatochrome effect, while the preferential solvation (PS) model is introduced in Chapter 3. The next two Chapters are for general information about ionic liquid (IL) and deep eutectic solvents (DES).

Chapter 6 intended to summarize the theoretical background of the applied molecular simulation techniques. Unfortunately, there are incorrect interpretations of fundamental concepts in molecular simulations here, just to give few examples: 'Generally, both these methods are being used to analyze the simulated system to **find** dynamic and thermodynamic properties (e.g., energy, pressure, volume, diffusion constant, thermal conductivity etc.)', 'The positions of atoms/molecules in the simulation box are **connected to find** the trajectories of

the atoms/molecules.', 'The equation $d^2r/dt^2=F_i/m_i$ is explained as 'and 2nd **derivative ratio** of r to t is the acceleration on particle i, ai.'. These examples create the impression that the writer of the thesis is unaware of these techniques.

Furthermore, Monte Carlo (MC) simulation is introduced in the same section even more detailed than molecular dynamics (MD) simulations, however there is no MC results in the thesis. Not to mentioned that the sentence about MC on Page 16 is simply incorrect ('In contrast, time independent of MC to calculate the properties related to time make it **less efficient** compared to MD.'), since MC discussed is solely a time-independent technique based on the description of the Monte Carlo (MC) method provided on the same page of the thesis. As such, it is impossible to compute time-dependent properties. Therefore, it is not a question of being 'less efficient,' but rather it is fundamentally impossible. Furthermore, there are sentences in Chapter 6, which is hard to link to any related topics ('The second reason is **nature of reactions** which is not needed to consider in very long distances. Therefore, **it is** critical to cut them and increase the speed of MD simulations.').

In the Results and discussion section, a diverse set of research topics are presented. In the first part, that is 'Solute-solvent, solvent-solvent interactions, ion delocalization, hydrogen bond interactions, and solvation structures', there is no proper introduction provided for why particularly these deep eutectic solvents systems were studied using MD techniques.

The title of the following section ('preferential solvation (PS) model by MD simulations') was a bit misleading since it is claimed that it is all about simulation results, but his own experimental results were also shown in Table 6 and partially discussed.

The next section entitled 'MD simulations in aqueous solutions of biochar for tetracycline sorption' seems like a short report rather than a discussion of the results, although the purpose of the study was mentioned properly.

In the fourth topics, NMR and DSC study of different ionic liquids (ILs) and low melting mixtures (LMMs) were presented with details of the experiments and setups.

In section 7.2, a thorough discussion on cellulose dissolution is presented, with a commendable introduction that clearly states the research objectives and incorporates a discussion on recently published results. However, there is some repetition of the force field expression and unnecessary technical details regarding the MD simulation, which could have been avoided. Nonetheless, the section effectively discusses some of the research findings and provides context for the research.

After reviewing the thesis, I have the following requests and questions for the discussion:

(1) Acceptor (AN) and donor normal (DN) constants are not defined in the thesis. Could you provide an explanation of their meanings and clarify how they can be obtained? (Page 2)

(2) In the thesis, it is mentioned that preferential solvation (PS) was measured for the aqueous solutions of ethaline. Could you provide detailed information on how the preferential solvation was precisely measured? Additionally, it is not clear from the thesis what $Y_1(\overline{\vartheta_1})$, $Y_2(\overline{\vartheta_2})$ and $Y_{12}(\overline{\vartheta_{12}})$ stand for? Explain it.

(3) The UV-Vis spectra were computed by TD-CAM-B3LYP/TZVP//B3LYP6-31G(d) level of theory for structures obtained by MD simulations. Can these spectra be compared directly with the experimental ones to elucidate solvatochromism?

(4) In relation to the discussion on cellulose dissolution, it is my understanding that intermolecular interaction energy plays an essential role in this phenomenon. Could you suggest which types of energetic properties would be suitable for calculation in order to gain a better understanding of this phenomenon?

In summary, based solely on scientometric evaluation, the PhD candidate has met the requirements of the doctoral school by having an adequate number of scientific publications to obtain a PhD. However, it appears that the PhD thesis may primarily serve a formal purpose. Nevertheless, considering the quality of the thesis, it is evident that further development in scientific communication is necessary for the PhD candidate to achieve the status of a truly independent researcher. Nevertheless, considering a successful defense, I recommend granting the PhD degree with 'rite' only.

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