Review of Ph.D. Thesis

"Cellulose dissolution: Comparison of two non-derivatizing solvent systems and the effect of additives"
presented by Mgr. Nikolay Kotov

The Ph.D. thesis of Mgr. Nikolay Kotov focuses on the acquisition of new experimental information on the changes of cellulose structure upon dissolution in two solvents, an ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl) and an organic solvent *N*,*N*–dimethylacetamide (DMAc) with lithium chloride (LiCl). FT-Raman, dispersive and attenuated-total-reflectance (ATR) FTIR spectroscopies have been utilized as the main tools for the detailed study. The studies were supplemented with complementary data obtained from other techniques such as wide-angle X-ray scattering (WAXS), solid-state NMR spectroscopy and dynamic light scattering (DLS).

The aims and objectives of the doctoral thesis to:
1) acquire information about the features of selected cellulose solvents;
2) investigate the changes in cellulose structure upon dissolution in the selected solvents; and
3) assess the influence of additives on cellulose dissolution;

have been achieved. It is found that water at low concentration (<3 wt%) acts as a co-solvent in cellulose-bmimCl mixtures. The presence of "Pluronics", has been shown to affect only cellulose in DMAc with LiCl at temperatures above 26 °C. The performed experiments, acquired information and conclusions undoubtedly lead to better understanding of cellulose dissolution processes and may lead to further advancements in cellulose processing and in preparation of new cellulose-based materials.

Thesis structuring:

The thesis comprises 6 chapters including concise but rather informative Introduction with detailed overview on cellulose structure and current state of knowledge in the field; Materials and Methods chapter; and chapters focused on the: Chapter 3: Characterization of the selected cellulose solvents, Chapter 4: Cellulose dissolution in DMAc-LiCl and in bmimCl and Chapter 5: Impact of Pluronics addition on cellulose dissolved in DMAc-LiCl and bmimCl. The thesis includes Final conclusion chapter which summarizes the whole work and critically discusses the findings with comparison to the current state of knowledge. Notably, the Candidate clearly states his own contributions within the performed work. I highly value the Candidate's ability to separate the results and discussion parts in each of the scientific chapters presenting the Thesis core work. This clearly shows the Candidate's proficiency on the matter and his critical assessment of available literature. However, I would have to point one weakness of the Thesis, and that is the absence of small conclusion Subchapters. In my opinion the conclusion subchapters should have been separated from the individual discussion parts of Chapters 3, 4 and 5.

Specific comments to the Thesis:

- Page 22 – Missing description of cellulose activation. In my opinion the citation to work of Raus *et al.* is not sufficient.
- Page 26 – Claim Microscope was used for analysis of heterogeneous samples. The Thesis should have reported the individual micrographs.
- Page 34 – Valuable DFT calculations have not been mentioned in the methods section.
- Page 45 – Unclear explanation: visually transparent, slightly colored viscous liquid
- Page 59 – The Author states that bmimCl is hydrophilic in nature. I would argue about this statement since the molecule has rather an amphiphilic character with the ion pair and hydrophobic tail.
- Typos, stylistic issues, number format – (Example: Page 51: crystallization of bmimCl crystallization; non-unified font size in Figures 11, 12 ,13; from Table 3 it was seen; Table 13 comma used as delimiter; Page 103 H-bond acceptor not accepter; etc.)
- Page 105 – I cannot imagine the flow of liquid under stationary conditions. Can the Author elaborate in detail what he meant with this statement?
- Referencing Tables or Figures several pages before they are actually presented. Example

- GA and AA conformers of bmimCl should have been presented.
- Page 115, Figure 28 – swapped spectra of cellulose and Pluronics.
- Page 119 – More specific explanation about planar and helix structure of PEO blocks.
- Generally the most of the presented figures were scaled with an unknown scaling factor. Maybe it would have been better to normalize the spectra for better representation (Example Figure 32)
- Why second derivative was not used for further analysis of spectra presented in Figure 32?
- Page 143 – Acquired data indicated increase in viscosity. Maybe it would have been beneficial to actually measure the viscosity.
- Presence of citations in Final conclusions chapter.
- No unified style of some references (Example: Dawsey, T. R. *et al.* 1990; Guo, J. *et al.* 2010)

The results of the Candidate are of high scientific quality. They are comprehensive, devoted to a clearly-defined topic, and with a potential overlap towards applications. The Candidate has been a co-author of 3 papers (1 first author) of high scientific visibility. The presented work clearly shows the Candidate's ability for creative scientific work.

Despite the formal issues such as typos and errors in the presented Thesis, I strongly support the candidacy of Mgr. Nikolay Kotov to present the work to the scientific board and defend the Ph.D. title under the study branch of Biophysics, chemical and macromolecular physics (4F4) at the Faculty of Mathematics and Physics, Charles University.

In Prague, May 3, 2018

Ing. Ognen Pop-Georgievski, Ph.D.
Dpt. Chemistry and Physics of Surfaces and Biointerfaces
Institute of Macromolecular Chemistry
Czech Academy of Sciences
Heyrovského nám. 2
162 06 Prague 6
Czech Republic

Specific questions to the Thesis:

1. Why the Author has chosen the second derivative for the analysis of the spectra? Wouldn't it be more beneficial to use the Fourier self-deconvolution instead?

2. The Author presents a torrent study on the dissolution of cellulose using an ionic liquid 1-butyl-3-methylimidazolium chloride (bmimCl) and an organic solvent *N*,*N*–dimethylacetamide (DMAc) with lithium chloride (LiCl). The conclusions from the thesis have indirect implications on the debate about Lindman's hypothesis. Can the Author philosophically access the ongoing debate on this hypothesis presented in the review by Glasser *et al.,* Cellulose (2012) 19:589–598, DOI 10.1007/s10570-012-9691-7?