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Review of Shinian Chang's PhD dissertation

“The role of entropy in the description of relaxation dynamics of ionic liquids”

Room temperature ionic liquids (ILs) have become one of the more promising materials for the development of advanced electrolytes in energy storage devices due to their desirable properties. That is why it becomes so important to thoroughly investigate their physical properties, including their relaxation dynamics and thermodynamic behaviour. Although the topic has been repeatedly undertaken in the last decades, not all aspects have yet been explored, for example the influence of the applied pressure on dynamic behaviour, as was mentioned in the preface to his doctoral dissertation by Shinian Chang.

Shinian Cheng's doctoral dissertation was carried out at the Institute of Physics of the Faculty of Science and Technology of the University of Silesia in Katowice under the supervision of Prof. Marian Paluch, an outstanding specialist in the field of research with the use of dielectric spectroscopy with a worldwide reputation. The subject of the work is part of the mainstream work of the team of Prof. Paluch and it concerns description of dynamics and thermodynamic properties of several ionic liquids. The title of the dissertation fully corresponds to the presented content.

The dissertation presented for evaluation takes the form of a collection of four thematically coherent, multi-author, original papers, published in the years 2020-2021 in renowned global scientific journals. They are collected together with the declarations of the co-authors in Appendix II. Such presentation of PhD work is permitted by the Act on academic degrees and academic title and on degrees and title in the field of art of 14.03.2003, where one can read that "*(...) doctoral dissertation may take the form of (...) a thematically*



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coherent set of articles published or accepted for publication in scientific journals (...)". These manuscripts were published in international scientific journals with the high impact factor IF from the JCR list. Two of them (one communication and one article) appeared in *The Journal of Chemical Physics*, one in the *Journal of Molecular Liquids*, and finally one in *The Journal of Physical Chemistry B*. In all these publications, the PhD student is indicated as the first author, which indicates his major involvement in the conduct of research, interpretation of obtained results and its description. The significant participation of the doctoral student is confirmed by the collected declarations of co-authors of these publications. Only for publication in *J. Phys Chem. B* the declarations of two co-authors are missing, but it should be noted that there are seven co-authors. I would also like to mention that in addition to the four works included in this dissertation, Shinian Cheng is the co-author of 10 other publications, which is certainly above average.

Although, due to the form of the work adopted by Shinian Cheng, the role of the reviewer as an evaluator is as limited as facilitated, because the evaluation of the originality and usefulness of the results and the way they are described have already been reviewed, in my opinion all four papers are very well prepared.

The first of the articles (*J. Chem. Phys.* **152** (2020) 091101) is devoted to the relation between molecular dynamics and configurational entropy S_c in room temperature ionic liquids. In this work, the authors tested the Adam-Gibbs model connecting molecular dynamics with configurational entropy for BMIm/TFSI (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). Authors found in the entire investigated supercooled liquid region a good agreement comparing the configurational entropy obtained by the combination of Vogel-Fulcher-Tammann (VFT) and Adam-Gibbs equations for rheological data with points determined directly from the calorimetric experiments. Glass transition temperature T_g determined on the basis of the obtained VFT equation is in good agreement with known from literature value obtained from the calorimetric experiment. This relatively short communication showing data for only one ionic liquid is very important because shows for the first time such approach for ionic liquids and promotes an understanding of the thermodynamic and dynamic properties of ILs and the relation between them.

Second article (*J. Chem. Phys.* **154** (2021) 044502) is devoted to similar correlation as the first one but results described in previous manuscript were compared with data obtained for two other imidazolium-based ionic liquids with longer aliphatic chain in cations. Additionally authors showed that the original Adam-Gibbs relation does not work when the

whole supercooled liquid state is considered and it was necessary to use generalized version proposed by Ozawa *et al.* with additional free parameter α . The parameter α as well as the isobaric fragility m_p , calculated from VFT equation, decrease with the elongation of alkyl chain attached to the imidazolium ring. Fact that $\alpha < 1$ for all investigated samples indicates that the configurational entropy is not sufficient to govern the ion dynamics. The authors also proved that for the tested ILs excess entropy S_e significantly exceeds the configurational entropy S_c and the difference between them becomes more pronounced with temperature increase. It must be noted here that Kauzmann temperature T_k estimated from extrapolation of temperature dependencies of both, S_e and S_c , give two values different by 8 deg. Additionally, for ILs the universal correlation between T_k and T_g is not maintained. For non-ionic glass-formers, the difference is generally within the range of 49÷61 deg., while for the tested ILs it is only about 18 deg. What's more interesting, despite this deviation from the norm, the authors proved that T_k for investigated materials is similar to the transition temperature to perfect glass T_o . It is a pity that the authors did not attempt to hypothesize on how to explain such behaviour.

Next two publications (*J. Mol. Liq.* **316** (2020) 113824 and *J. Phys. Chem. B* **124** (2020)1240) describe universal scaling behaviour of entropy and conductivity in ionic liquids. In first of them authors investigated the density scaling behaviour of dc-conductivity and entropy of 1-ethyl-3-methylimidazolium diethylphosphate over a broad range of temperatures, pressure and volume. Additionally, authors investigated 15 other ILs with different structure, both cation and anion, what allowed to determine influence of the strength of intermolecular interactions on some physical parameters. Second paper shows comparison of properties for two ILs with similar chemical structure but with different molecular weight. One of them was low molecular weight and second one macromolecular ionic liquid. Both type of ILs show some similar behaviour – the entropy scaling exponent being the Grüneisen parameter is a linear function of entropy. The Grüneisen parameter depends strongly on physical interaction. Again, it would be useful if the authors at least proposed a hypothesis behind such behavior. However, these works demonstrate how physicochemical properties of ILs can be predicted for conditions beyond those measurements, what has obvious utility in the design and development of new products and applications.

The Appendix II, included described above publications, is preceded by the abstracts in English and Polish, and a 58-page document written in English, which consists of six subchapters and Appendix I. In the first three sections, compiled on the basis of 79 references,

the basic knowledge necessary to understand the topic under study is presented. They include an introduction to ionic liquids, some aspects of the glass transition, and methods of linking entropy with molecular dynamics. Although this part is only 20 pages, it presents the most important definitions and models used in the analysis of the presented in next sections experimental results.

The fourth section describes the experimental techniques and materials used in the work. In the fifth chapter the PhD student briefly presented the results and their discussion, and in the last subsection he briefly summarized the entire dissertation. After the summary, there is a reference list with 118 positions and Appendix I with graphs showing the results from standard and modulated differential scanning calorimetry for chosen materials as well as the *PVT* data for two samples. The experimental part of the dissertation shows the results described in the manuscripts constituting Appendix II, so it is not necessary to repeat description. What is striking, however, that here there is no references whatsoever to these publications. In my opinion, such a reference to the works should be found here. Apart from the formal requirements that references should be made each time the work has already been published, it would simply greatly facilitate reading and verification of the work submitted for evaluation. The list of used symbols would also make reading the work much easier.

The lack of reference to the publications constituting the main part of the doctoral dissertation and the lack of bolder hypotheses trying to explain the observed similarities and differences to classic non-ionic glass-formers are, in my opinion, the main disadvantages of this work.

The work of Shinian Cheng presented for review undoubtedly has a very high cognitive value and makes a significant contribution to the development of the discipline. The minor critical remarks contained in the review do not in any way undermine the main achievements presented in the dissertation and may not significantly affect its assessment. Summing up, I evaluate this thesis positively and I state that the submitted dissertation of Shinian Cheng meets the requirements set out in the Act on academic degrees and academic title and on degrees and title in the field of art of March 14, 2003 (Journal of Laws 2003 No. 65, item 595, as amended). Therefore, in my opinion, Shinian Cheng can be admitted to further procedures necessary to obtain the PhD degree. In addition, taking into account the very high substantive level of the doctoral dissertation itself and the outstanding scientific achievements of the PhD student, I am asking for a distinction of the reviewed work.

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