



Lodz University of Technology

Department of Molecular Physics

Łódź, 20.09.2023

Dr hab. Lidia Okrasa

e-mail: lidia.okrasa@p.lodz.pl

tel. +48 42 6313286

Review of Beibei Yao's PhD dissertation

“The Liquid-Liquid Phase Transition in Ionic Liquids at Ambient and Elevated Pressure”

Beibei Yao's doctoral dissertation was completed at the Institute of Physics, Faculty of Science and Technology, University of Silesia in Katowice, under the supervision of Dr. hab. Żaneta Wojnarowska, an outstanding specialist in the field of molecular dynamics research and charge transfer mechanisms in ionic liquids. The title of the dissertation fully corresponds to the presented content. As mentioned in the introduction to Beibei Yao's doctoral dissertation, liquids play an important role in our lives, which is why it is so important to understand the transitions that occur during changes of temperature and pressure. The work focuses on the study of the liquid-liquid transition (LLT), which has not yet been fully explored. To thoroughly investigate the liquid-liquid transition, Beibei Yao selected twenty (tetra)alkylphosphonium based ionic liquids (IL) with different cations and anions. In the research, the doctoral student used many complementary techniques, but the leading ones were: differential scanning calorimetry (DSC) and dielectric measurements.

The dissertation presented for evaluation takes the form of a collection of four thematically coherent, multi-author, original papers, published in the years 2022-2023 in renowned global scientific journals. The publications that make up Beibei Yao's doctoral dissertation are:

1. *Tailoring Phosphonium Ionic Liquids for a Liquid-Liquid Phase Transition*, Beibei Yao, Marian Paluch, Mateusz Dulski, Courtney Quinn, Shannon McLaughlin, Anne McGrogan, Malgorzata Swadzba-Kwasny, and Zaneta Wojnarowska, *J. Phys. Chem. Lett.*, **14**, 2958-2964 (2023),



Department of Molecular Physics

90-924 Poland, Lodz, 116 Zeromskiego Street, building A27

phone +48 42 631 32 05, fax +48 42 631 32 18,

www.kfm.p.lodz.pl, www.p.lodz.pl

2. *Pressure induced liquid-liquid transition in a family of ionic materials*, Zaneta Wojnarowska, Shinian Cheng, Beibei Yao, Malgorzata Swadzba-Kwasny, Shannon McLaughlin, Anne McGrogan, Yoan Delavoux, and Marian Paluch, *Nat. Commun.*, **13**, 1342 (2022),
3. *Effect of bulky anions on the liquid-liquid phase transition in phosphonium ionic liquids: Ambient and high-pressure dielectric studies*, Beibei Yao, Marian Paluch, and Zaneta Wojnarowska, *Sci. Rep.*, **13**, 3040 (2023),
4. *Self-assembled nanostructures in aprotic ionic liquids facilitate charge transport at elevated pressure*, Beibei Yao, Marian Paluch, Jaroslaw Paturej, Shannon McLaughlin, Anne McGrogan, Malgorzata Swadzba-Kwasny, Jie Shen, Beatrice Ruta, Martin Rosenthal, Jiliang Liu, Danuta Kruk and Zaneta Wojnarowska, *ACS Appl. Mater. Interfaces* **15**, 39417-39425 (2023) – marked in the thesis still as “under review”.

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 coherent set of articles published or accepted for publication in scientific journals (...)". These manuscripts were published in international scientific journals with high impact factor IF from the JCR list (4.6 ÷ 16.6). They are also highly scored by the Ministry of Education and Science (three publications have 200 points each and one publication has 140 points). In three of these publications, the doctoral student is the first author, which indicates her great involvement in conducting research, analysis and interpretation of the obtained results, and their description. The significant participation of the doctoral student is also confirmed by the collected declarations of the co-authors of these publications. The declarations show that Beibei Yao planned, carried out the experimental work (except for Raman studies, small- and wide-angle X-ray scatterings, Nuclear Magnetic Resonance measurements), analysed the data, prepared figures and co-wrote all four manuscripts. I would also like to mention that in addition to the four papers included in this dissertation, Beibei Yao is a co-author of 5 other publications as well as two oral and one poster presentations on scientific conferences. This clearly proves the doctoral student's above-average involvement in research work.

Beibei Yao's dissertation has 179 pages and, apart from acknowledgments and summaries in English and Polish, contains 9 chapters. In the first two chapters, she briefly described in 20 pages her motivation for the undertaken research, as well as the theoretical background needed to understand the entire work. In the third chapter, she presented the tested materials and used research techniques, with a concise description of how to analyse



and interpret the obtained results. The next four paragraphs contain a text of the publications being the basis of this dissertation, along with Supplementary Information, preceded by the reprint of publication headline and declarations of all co-authors. The doctoral dissertation ends with a Conclusion and Appendix. It is difficult to determine how many literature references were cited in the work, because each chapter ends with a separate list, but I estimate that there are about 150 items.

Although, due to the form of the work adopted by Beibei Yao, 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 (*The Journal of Physical Chemistry Letters*, **14** (2023) 2958-2964) is devoted to the study of the influence of cation self-assembly on the ion dynamics in the vicinity of liquid-liquid and liquid-glass transitions of ten tetra(alkyl)phosphonium ionic liquids. It was found that nonpolar local domains formed by 14-carbon alkyl chains are crucial in obtaining two supercooled states of different dynamics within a single ionic liquid. DSC measurements confirmed that when the length of all alkyl chains in cations was shorter than 14 the transition liquid-liquid was not observed. This behaviour was independent on used anion ([TFSI]⁻ or [Cl]⁻). At least one alkyl group in the cation had to be long enough for a LLT to be evidenced by calorimetric measurements, even though nanoordering, confirmed by Raman spectroscopy, still occurs for shorter alkyl chains. Interestingly, the temperature and enthalpy of liquid-liquid transition depended strongly on the lengths of the remaining three alkyl groups. The publication also describes the results of dielectric spectroscopy for this group of materials. They confirmed that for samples containing a long 14-carbon alkyl group in the cation liquid-liquid phase transition could be observed, as indicated by the significant deviation of the ion dynamics (τ_σ , σ_{dc}) from the Vogel-Fulcher-Tammann (VFT) behaviour. However, analysis of the dielectric data in terms of the Stickel operator gave somewhat similar results (negative deviation from the linear regime at high temperature) for all tested samples. Therefore, it can be assumed that shortening the aliphatic chain reduces the possibility of LLT, but maintains the potential of IL for partial nanoorganization.

Second article (*Nature Communications*, **13** (2022) art No. 1342) is devoted to investigation of LLT in series of seven ionic liquids containing trihexyl(tetradecyl) phosphonium cation [P_{666,14}]⁺ and anions of different size, geometry, conformational flexibility and coordinating ability. This work contains a huge amount of information. It presents not only a thorough calorimetric analysis of the tested materials (the influence of



the heating rate on the transition temperatures, the influence of annealing on the occurrence of physical aging, the influence of used anion on the LLT temperature), but also the results of dielectric tests under normal and elevated pressure, which clearly have a significant impact to change the ion dynamics. To sum up, this work showed: (1) a heating rate influences the transition temperatures, (2) annealing below the T_g results in an endothermic peak of physical aging, (3) the temperature of liquid–glass transition remains constant for studied ILs, (4) the temperature of liquid-liquid transition decreases with decreasing basicity and increasing van der Waals volume of the anion, too large and/or rigid anions prevent the LLT, (5) size and character of anion influence on crystallization/melting behaviour, (6) results of calorimetric and dielectric measurements are compatible, (7) the parameters characterizing the ion dynamics ($\tau\sigma$, σdc) and distribution of relaxation times (βKWW) monitored on isobaric cooling and isothermal compression reveal peculiar behaviour at the LLT, (8) high-pressure experiment allows the estimation of very small volume changes accompanying LLT, undetectable in conventional dilatometry measurement.

Third manuscript (*Scientific Reports*, **13** (2023) art No. 3040) extends the results described in the previous work about two more materials with other anions: bis(1,4,4-trimethylpentyl)phosphinate [BTMPP]⁻ and bis(2-ethylhexyl)phosphate [BEHP]⁻ with the same as previously cation [P_{666,14}]⁺. These anions are non-cyclic and consist of two long and branched alkyl chains connected to a phosphorus core. Such structure of anions may affect the LLT. And indeed, the calorimetric results only indicated the occurrence of the typical glass transition in examined ILs and did not provide any signs of the first-order liquid–liquid transition. Also, the dielectric parameters did not reveal any signs of LLT. However, after further careful analysis and comparison of the results with those obtained for other materials described in the previous work, a unique phenomenon called inflection point was discovered in the case of [P_{666,14}][BTMPP], which characterizes the high-pressure dynamics of ionic systems with hidden LLT. The calorimetric and dielectric measurements were extended in this work by viscosity and density measurements.

In last manuscript (*ACS Applied Materials & Interfaces*, **15** (2023) 39417-39425) the authors focused on the charge transport mechanism of three phosphonium ionic liquids: two materials previously described in the second publication ([P_{666,14}][SCN], [P_{666,14}][TCM]) to another newly synthesized one ([P_{666,14}][DCA]). All tested materials contained the same large amphiphilic cation with long, intertwined nonpolar alkyl chains and much smaller anions. In this work, calorimetric and dielectric investigations were extended about viscosity tests, MD simulations, WAXS, SAXS and NMR measurements, which gives a broader



picture of the tested materials. The studies showed that upon isothermal compression and isobaric cooling, the studied phosphonium ILs transform from one liquid state to another, both differing in self-assembly behaviour, viscosity, and charge transport mechanism. The comparative analysis showed that in liquid 1 (at $T > T_{LL}$ and $P < P_{LL}$) the charge transport is fully controlled by the viscosity, but in liquid 2 long alkyl chains of cations are partially frozen in nonpolar domains, while anions move quickly through the created channels regardless of structural dynamics. Such a self-organized nanostructure of liquid 2 can be precisely adjusted by appropriate selection of the thermal/pressure history, as well as the structure and size of anions, obtaining materials that differ in their charge transport mechanism, what may have a huge impact on new technologies related to ionic liquids as soft conductive materials.

As I mentioned earlier, the results of the research described in four publications were summarized by Beibei Yao in Chapter 8 in the form of answers to 11 well-formulated questions that cover the most important aspects of her work. To say what is most important in this dissertation, it would be enough to say that it was the answer to these very aptly formulated questions, because in the answers to them the doctoral student summarized her entire achievement. I will mention here only the most important ones in my opinion. In her work, the PhD student described how the presence of a liquid-liquid transition in ionic liquids can be experimentally proven, with particular emphasis on dielectric spectroscopy (dielectric fingerprints accompanying LLT), and based on the study of 20 different materials, she described how in a selected family of ionic liquids the phase transitions are influenced by the structure of both cation and anion, as well as by the thermal history of the samples and the applied pressure. In addition, she answered the question what is the mechanism of charge transport in ionic liquids below and above the liquid-liquid transition and how this transfer is influenced by the applied pressure.

I must admit that the dissertation is very clear, well-written, and above all, it contains a description of all the elements needed to understand this work. It could itself be a great teaching material for people working in the domain of ionic liquids, especially in the study of their dynamics. However, it is not devoid of some minor shortcomings and inaccuracies that would require correction or supplementation, mainly in the theoretical introduction. On page 20, the PhD student wrote that the glass transition temperature is usually defined at structural relaxation time $\tau_{\alpha}(T_g) = 1000s$. It is only one of possibilities. The most often, a relaxation time of 100s is used to estimate T_g , similarly as in the case of conductivity data analysis described on page 37. This should be clearly mentioned here and



described what effect using different relaxation times to estimate T_g may have. I found the second understatement in this study on page 18, where it is described that T_g is usually determined as the midpoint of the transition region. This method of determining T_g is consistently repeated on page 34 in the description of the DSC technique. There is no error in this, especially since the glass transition temperature actually determined in this way is comparable to the data obtained using dielectric spectroscopy, but it should be remembered that very often, and in recent years more and more often, another method of T_g determining from DSC curves is also used, namely, as the beginning of the transition, the so-called onset point. This should be especially remembered when comparing own results with those in the literature. I have no doubt that the doctoral student is aware of this fact, but perhaps it would be good to mention it here. These two aspects, without further explanation, can be misleading, especially for someone unfamiliar with this type of research. I also found a few editorial errors in the work, such as the double use of the term "cold crystallization" instead of "cold crystallization" on page 34, or TLL instead of T_{LL} on page 88. And the last editorial note is that it would be good if the figure captions included on the same page as the drawing, which would make reading easier. This is all the more misleading because the text of figure captions does not differ in style from the main text of the work. Of course, this shortcoming was not in the original text of the publication.

The work of Beibei Yao presented for review undoubtedly has a very high cognitive value and makes a significant contribution to the development of the discipline. Summing up, I evaluate this thesis positively and I state that the submitted dissertation of Beibei Yao 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, Beibei Yao 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.

Eidia Olwa

