Prof. dr hab. Adam Patkowski
Uniwersytet im Adama Mickiewicza
Wydział Fizyki
Zakład Biofizyki Molekularnej
ul. Uniwersytetu Poznańskiego 2
61-614 Poznań
Tel: +48-61-8295262
E-mail: patkowsk@amu.edu.pl

Report on the PhD thesis:

"The Liquid-Liquid Phase transition in Ionic Liquids at Ambient and Elevated Pressure" by Ms. Beibei Yao

The dissertation of Ms Beibei Yao consists of (i) four multi-author publications in which the individual contribution of the Author can be extracted and (ii) additional introduction, description of systems studied and methods used and extended conclusions. The Author included in her thesis the statements of all the co-authors in which their individual contributions are defined. She also defined her individual contribution to each of the publications in terms of work performed. The statements of the Author are consistent with the statements of all other co-authors. Thus, the formal requirements: (art. 187 Ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2018 r. poz. 1668 z uzup.)) concerning the form of the PhD thesis were fulfilled.

The publications composing the PhD thesis of Ms. Beibei Yao are:

1. **Beibei Yao**, Marian Paluch, Mateusz Dulski, Courtney Quinn, Shannon McLaughlin, Anne McGrogan, Malgorzata Swadzba-Kwasny, and Zaneta Wojnarowska, *Tailoring Phosphonium Ionic Liquids for a Liquid–Liquid Phase Transition*, J. Phys. Chem. Lett.,14, 2958-2964 (2023)
2. Zaneta Wojnarowska, Shinian Cheng, **Beibei Yao**, Malgorzata Swadzba-Kwasny, Shannon McLaughlin, Anne McGrogan, Yoan Delavoux, and Marian Paluch, *Pressure-induced liquid-liquid transition in a family of ionic materials*, Nat. Commun., 13,1342 (2022)
3. **Beibei Yao**, Marian Paluch, and Zaneta Wojnarowska, *Effect of bulky anions on the liquid-liquid phase transition in phosphonium ionic liquids: Ambient and high-pressure dielectric studies*, Sci. Rep., 13, 3040 (2023)
4. **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, *Self-assembled nanostructures in aprotic ionic*

liquids facilitate charge transport at elevated pressure, ACS Appl. Mater. Interfaces, under review.

The contributions of Ms. B. Yao to all the publications can be separated. In all 4 publications Ms. B. Yao planned and carried out the experimental work, analyzed the data, prepared figures, and co-wrote the manuscript. In publication [2] her activities were sheared with Mr. S. Cheng and in publication [3] she additionally conceived the study. I understand that the contributions of Ms. B. Yao were related mainly to the BDS and DSC experiments. In publications [1, 3, 4] Ms. B. Yao is the first author.

Additionally, she was a co-author of 5 publications not related to her PhD thesis (the first author in one of them) in leading scientific journals, two oral presentations and one poster at international conferences.

Despite many years of experimental and theoretical studies the physical nature of supercooled liquids and the liquid-glass transition is not fully understood. One of the interesting features of these liquids is the first order liquid-liquid transition (LLT) which was observed in several systems. This is a transition between two supercooled liquid states which differ in local structure, density as well as dynamic and thermodynamic properties. The existence of the LLT makes the physical understanding of the supercooled state even more difficult. The interpretation and universality of the LLT remains controversial. From the theoretical point of view the occurrence of LLT requires cooperative formation of local ordered structures. It is suggested that LLT can be observed in every liquid.

A very interesting class of glass-forming liquids are the ionic liquids (ILs) which due to their exceptional features, microstructural organization (resulting from different intermolecular interactions) and transport properties offer possible applications in basic science and technology. They can be potentially applied as advanced electrolytes in batteries and energy storing devices where the most important parameter is the ion dynamics which has been studied mainly as function of temperature (T) under atmospheric pressure.

The aim of this PhD thesis is a systematic study and characterization of a series of ILs that exhibit the LLT in terms of their thermodynamic properties and ion dynamics in the vicinity of the LLT at ambient and elevated pressures. The motivation and the aim of the PhD studies is discussed in detail in the Introduction.

In chapter 2 the theoretical background of the planned research work is presented. It contains the description of the liquid state and the LLT, the justification of the choice of ILs to study the LLT and the description of the thermodynamics and dynamics of ILs at ambient and high pressure.

In chapter 3 the experimental details and detailed research plan of the studies are discussed. For her studies Ms. B. Yao selected twenty (tetra)alkylphosphonium – based ILs with different cations and anions which structure and basic physical parameters are given tn Table 3.1. The cations $[P_{mmm,n}]^+$ consist of three short alkyl chains of different length m (from 4 to 6) and one long chain of length n (from 2 to 14). The selected anions were $[TFSI]^-$, $[Cl]^-$, $[BH_4]^-$, $[BF_4]^-$, $[Dec]^-$, $[SCN]^-$, $[DCA]^-$, $[TAU]^-$, $[BOB]^-$, $[BTMPP]^-$ and $[BEHP]^-$.
In experimental studies the main experimental methods were Differential Scanning Calorymetry (DSC) – used to identify the glass transition, LLT, cold crystallization and melting processes and Broadband Dielectric Spectroscopy (BDS) at ambient and high pressure – applied to obtain relaxation and conductivity spectra of ILs. Supplementary measurements were performed by means of: Rheology – to obtain viscosity and dynamic shear modulus, Densitometry, Raman scattering – to monitor conformational changes of alkyl chains of ILs, X-Ray Diffraction (XRD, both SAXS and WAXS) – to investigate local ordering, molecular arrangement and phase transitions in ILs. Also molecular dynamics (MD) simulations were performed to verify the charge transport mechanisms in ILs. The physical principles, experimental conditions and methods of data interpretation are described in detail for DSC and BDS and briefly for other methods in chapter 3.

I understand that the main contribution of Ms. B. Yao to the experimental work, according to the all authors' declarations, is related to the DSC and BDS methods.

The experimental results of the PhD thesis are described in chapters 4-7 where the text of the publications [1-4] is reprinted together with the declaration of all authors describing their specific contribution to each publication.

In chapter 4 publication [1] is presented. In this work the effect of cation self-assembly on ion dynamics in the vicinity of liquid-liquid and liquid-glass transitions of tetraalkylphosphonium ILs ($[P_{mmm.n}]^+$ (m: 4 and 6, n: 2-14). In these studies DSC, BDS, and Raman spectroscopy were used. The chemical analysis of the samples was performed by means of X-ray fluorescence (EDXRF), NMR and TOF mass spectroscopy.
In the literature it has been shown that the LLT occurs in ILs composed of $[P_{666,14}]^+$ cation and $[BH_4]^-$, $[TFSI]^-$, $[TCM]^-$ and $[SCN]^-$ anions due to formation of local structures by the amphiphilic posphonium cations.

The question studied in publication [1] was what combination of alkyl chain lengths of phopsphonium ILs results in formation of heterogeneous microstructures and LLT. Two groups of phosphonium ILs were synthesized: (i) $[P_{mmm.14}]^+$ cation (m: 4, 6) with $[TFSI]^-$ and $[Cl]^-$ anions, and (ii) $[P_{666,n}]^+$ (n: 2, 4, 6, 8, 12) combined with $[TFSI]^-$ and $[Cl]^-$ anions. Based on the DSC diagrams it was shown that the LLT occurs in ILs of group (i) but not group (ii), so n=14 is necessary to induce the LLT. The change of the lengths of the three short chains from m=6 to 4 results in an increase of the enthalpy of the LLT and T_{LL} temperature. Temperature dependence of the conductivity relaxation time τ_σ and dc-conductivity σ was measured for chloride and TFSI salts of $[P_{444,14}]^+$ and $[P_{666,14}]^+$ (ILs with LLT) and $[P_{666,n}]^+$ based (n: 2-12) (ILs without LLT) by means of BDS. It was shown that the LLT is clearly visible in the Stickel plot, where the Stickel operator exhibits a minimum which is not present in corresponding data of ILs without LLT. Raman spectroscopy was used to study the morphology of two ILs with and two ILs without LLT. The Raman spectra revealed alkyl chain coupling due to their mutual ordering for ILs both with and without LLT.

Thus, in publication [1] it was shown that local arrangement of alkyl chains is observed in all studied phosphonium ILs regardless of LLT. Characteristic features of ILs with LLT is an endotherm peak in the DSC heating scan and characteristic changes in temperature dependence of τ_σ and σ_{dc} at T_{LL}. These findings allow to select tetraalkyl phosphonium ILs with LLT.

Next step in the PhD research of Ms. B. Yao (publication [2]) was the investigation of the effect of the size and shape of the anions and high pressure in the $[P_{666,14}]^+$-based ILs on their dynamics in the vicinity of the LLT. Six anions of different size, geometry, conformational flexibility and coordinating ability were selected. It was shown that LLT occurs in phosphonium based ILs with $[TCM]^-$, $[TFSI]^-$, $[TAU]^-$, $[BH_4]^-$ and $[SCN]^-$ anions but not with $[BF_4]^-$ anion which shows cold crystallization. T_g temperature is comparable in all studied ILs but the T_{LL} temperature is decreasing with increasing anion size. BDS was used to determine the dynamic parameters τ_σ and σ_{dc} and the distribution of relaxation times measured by the β_{KWW} exponent on isobaric cooling and isothermal compression. It was found that $\tau_\sigma(T_{LL}, P_{LL})$ is constant for a given liquid and the τ_σ relaxation times are strongly elongated at T_{LL} and their distribution becomes broader (β_{KWW} decreases).

In publication [3] the effect of bulky phosphorous-based anions with long alkyl chains ($[BEHP]^-$ and $[BTMPP]^-$) on the LLT in phosphonium ILs containing $[P_{666,14}]^+$ cation was studied at ambient and high pressure. In the previous publication [2] it was postulated that large anions in phosphonium-based ILs prevent the LLT because they disturb the ordering of the alkyl chains in the non-polar domains. Such ordering is required for the LLT to occur in these ILs. The DSC scans for both ILs exhibit a clear liquid-glass transition but no LLT. The conductivity relaxation process was studied by means of BDS and a characteristic behavior of

ILs was found with no sign of LLT. However, the analysis of the dielectric and viscosity data using the VFT equation and Stickel plot have shown that although the Stickel plot is linear for $[BEHP]^-$ anion, it is not linear for $[BTMPP]^-$ anion and its shape resembles that of the IL with $[BOB]^-$ anion, which in the previous publication [2] was described as IL for which the LLT overlapped with the liquid-glass transition. Additionally, a concave-convex behavior (called the inflection point) was found for the $\log\tau_\sigma(P)$, similar to that observed in $[P_{666,14}][BOB]$ IL. It was suggested that such a behavior is characteristic for high pressure data with hidden LLT. Thus, in publication [3] it has been shown that the expectation that bulky anions hinder the LLT in $[P_{666,14}]^+$-based ILs is not always fulfilled.

The last part of the PhD thesis concerns studies of the charge-transport mechanism through the self-assembled nanostructures and the effect of high pressure (publication [4] – under review). Three ILs of the same cation $[P_{666,14}]^+$and anions of different size and shape: $[SCN]^-$, $[DCA]^-$ and $[TCM]^-$ were used. A combination of complementary methods: DSC, BDS, viscometry, SAXS and WAXS, NMR relaxometry and MD simulations was applied. DSC measurements revealed the presence of the LLT and two liquids: liquid1 and liquid2 in all three ILs. XRD studies of the IL with the $[DCA]^-$ anion on cooling and subsequent heating corroborated the existence of the LLT and two liquid states. The charge-transport mechanism in the vicinity of the liquid-liquid and liquid-glass transitions was studied by means of BDS. It was shown that the temperature dependence of the conductivity relaxation time τ_σ obeys the VFT law in liquid1 and changes to Arrhenius behavior in liquid2 below T_{LL} with a higher activation energy. In the glassy state below T_g the dependence remains of Arrhenius-type but with a lower activation energy. The structural relaxation times τ_α were measured by means of TMDSC and rheology for IL containing $[DCA]^-$ anion. The structural τ_α and conductivity τ_σ relaxation times were compared. In liquid1 these two times were almost identical indicating that the charge-transport mechanism relies on the diffusion of molecular subunits (vehicle mechanism) and is controlled by viscosity of the system. Below T_{LL} in liquid2 τ_α becomes slower than τ_σ. The divergence of the times measured by parameter $R=\log[\tau_\alpha(T_g)/\tau_\sigma(T_g)]$ amounts to about 3 for all studied ILs. It was explained by the fact that τ_α in liquid2 is mainly due to the relaxation of the skeleton formed by the long alkyl chains of the cation and the charge transport results from relatively fast movement of the anion through the formed channels. This model was corroborated by the measurements of translational diffusion of the cation in liquid2 of $[P_{666.14}][DCA]$ IL by means of ^1H NMR relaxometry. It was shown that D_{trans} of the cation slows down at T_{LL} and remains practically constant at lower temperatures.

High pressure BDS measurements in combination with MD simulations showed that the nanostructure of the $[P_{666,14}]^+$cation domains depends of the anion size and pressure and diffusion of anions becomes faster with increasing pressure. Thus, in the studied ILs the fast charge transport below T_{LL} is decoupled from structural relaxation and viscosity, is pressure tunable and depends on the anion size and thermal history of the sample.

In chapter 8 (Conclusion) all the important results of the thesis are discussed in detail (11 pages) and put in perspective of the literature. Also a short outlook is presented.

The studies presented in this thesis belong to the leading themes in the field of the nanostructure and conductivity of ionic liquids and the liquid-liquid transition.

The content of the thesis closely corresponds to the title.

In my opinion the most important new achievements and conclusions of this Ph.D. thesis are:

- systematic studies of the LLT in a series of phosphonium-based IL showing the effects of the structure of cation and anion on the LLT,
- evidence that the aliphatic chain length C_{14} of the $[P_{mmm,14}]^+$ cation is crucial for formation of nonpolar ordered domains and the occurrence of the LLT,
- showing that below the LLT in liquid2 structural and conductivity relaxation times decouple and suggesting an ion transport mechanism,
- showing that different anions result in different pressure effects on the ion transport and nanostructure of liquid2.

All the new and very interesting results are critically discussed in the framework of available models and compared with literature. The obtained results are very important for a better understanding of the relationship between the dynamics, nanostructure and thermodynamics of ILs and the nature of the charge transport mechanisms in these materials.

The first introductory part of the PhD thesis (pages 10-42) which consists of introduction to the physics of ILs, the liquid-liquid and liquid-glass transitions, the description of phenomenological models used in data analysis and the experimental techniques used to obtain the data is very well organized and written and indicates a very broad and deep Author’s understanding of the field of ILs and the LLT. This part will be very useful even for a reader less experience in the field. Reading this part we can fully appreciate the Author’s general knowledge in the field.

In the course of her PhD studies Ms. Beibei Yao became an expert in thermodynamic description of the dynamics of supercooled ILs, the LLT as well as dynamic and thermodynamic methods used to obtain the data in a broad T-P range. As a graduate student she showed herself to be a very talented and hard working person with high theoretical and experimental skills able to solve independently scientific problems. She has also demonstrated a high ability to work with others.

The scientific value of the presented PhD thesis is very high. The author addressed important questions in the field of ILs and the LLT, obtained very interesting, new and important results. All this led to important conclusions concerning the role of chemical composition and microstructure in relaxation dynamics and the LLT of selected class of ILs. I have no doubt that the new very interesting results obtained by the Candidate essentially broaden our knowledge and understanding on the relation of the LLT to structural, dynamic and thermodynamic parameters of glass forming ILs.

I am fully convinced that the PhD thesis "The Liquid-Liquid Phase Transition in Ionic Liquids at Ambient and Elevated Pressure" by Ms Beibei Yao fulfills all the formal and scientific requirements (art. 187 Ustawy z dnia 20 lipca 2018 r. Prawo o szkolnictwie wyższym i nauce (Dz. U. z 2018 r. poz. 1668 z uzup.)) and I recommend to proceed with the further stages of the procedure necessary to obtain the PhD degree.

At the same time I apply for distinction of this doctoral dissertation.

Justification

The PhD thesis of M. Sc. Beibei Yao consists of 4 multi-author publications published in high quality scientific journals. In three publications Ms. Beibei Yao is the first author. Thus, her contribution to these publications is dominant.

Additionally, she was a co-author of 5 publications not related to her PhD thesis in leading scientific journals. She is a very active scientist involved in a very high quality scientific research. I am fully convinced that her PhD thesis deserves the distinction.

Poznań, September 20, 2023.

Prof. dr hab. Adam Patkowski