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

by **M. Sc. Shinian Cheng**

The dissertation of Mr. Shinian Cheng 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 discussion of the results. The Author included in his thesis the statements of all the co-authors in which their individual contributions are defined. He also defined his 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 Mr. Shinian Cheng are:

1. **Shinian Cheng**, Małgorzata Musiał, Żaneta Wojnarowska, and Marian Paluch, *The relation between molecular dynamics and configurational entropy in room temperature ionic liquids: Test of Adam-Gibbs model*, J. Chem. Phys. 2020, 152, 091101.

He was one of the corresponding authors.

His contribution was: conceiving the study, planning the experimental work, analyzing experimental data, discussing the results, writing the manuscript and preparing the figures.

2. **Shinian Cheng**, Małgorzata Musiał, Żaneta Wojnarowska, K.L. Ngai , Johan Jacquemin and Marian Paluch, *Universal scaling behavior of entropy and conductivity in ionic liquids,* J. Mol. Liq. 2020, 316, 113824.

He was one of the corresponding authors.

His contribution was: conceiving the study, planning the experimental work, participating in the literature review, analyzing experimental data, discussing the results, writing the manuscript and preparing the figures.

3. **Shinian Cheng**, Żaneta Wojnarowska, Małgorzata Musiał, and Marian Paluch, *Correlation between configurational entropy, excess entropy, and ion dynamics in imidazolium-based ionic liquids: test of Adam=Gibbs model,* J. Chem. Phys. 2021, 154, 044502.

He was one of the corresponding authors.
His contribution was: conceiving the study, planning and carrying out the experimental work, analyzing experimental data, discussing the results, preparing the figures, and writing the manuscript.

4. **Shinian Cheng**, Małgorzata Musiał, Żaneta Wojnarowska, Adam P. Holt, Charles M. Roland, E. Drockenmuller, and Marian Paluch, *Structurally related scaling behavior in ionic systems*, J. Phys. Chem. B 122020, 124, 1240.

His contribution was: conceiving the study, planning the experimental work, carrying out the dielectric experiments, analyzing experimental data, discussing the results, preparing the figures, and writing the manuscript.

In all four publications Mr. Shinian Cheng is the first author and in the first three of them – one of the corresponding authors. His contributions can be separated and consisted of: conceiving the study, planning (and carrying out in [3, 4]) the experimental work, analyzing experimental data, discussing the results, preparing the figures, and writing the manuscript. Additionally, he was a co-author of 10 publications not related to his PhD thesis (the first author in three of them) in leading scientific journals.

A relatively new class of ionic conductors – ionic liquids (ILs) became a significant class of materials due to their properties and potential applications as advanced electrolytes in batteries and energy storing devices. A very significant parameter for their practical applications is the ion dynamics which has been studied mainly as function of temperature (T) under atmospheric pressure . In such studies both the thermal energy and density are changing and their effect on molecular dynamics cannot be separated. Only additional studies of the effect of pressure (P) at constant T allow to determine the separate effect of density.

The aim of the PhD thesis was to investigate the ion dynamics in selected ILs over a broad T-P range both in the normal and supercooled liquid region and, additionally, using the PVT and heat capacity data to determine the relationship between the dynamic processes and thermodynamics of the ILs.

For this study the Author selected a series of aprotic ILs of a good glass forming ability, among them one polymeric IL.

Complementary methods were used to obtain the dynamic and thermodynamic data of these materials. The conductivity of the ILs, in a broad T-P range, was measured by means of broadband dielectric spectroscopy (BDS). Additionally, rheology, differential scanning calorimetry (DSC), temperature modulated DSC (TMDSC) and PVT measurements were performed in order to obtain viscosity, glass transition temperature, specific heat and specific volume, respectively.

In chapter 1 the definition and fundamental properties of ILs are presented.

In chapter 2 different aspects of the supercooled liquids and the glass transition are discussed. In particular the thermodynamics and dynamics of supercooled liquids is presented and relevant parameters and their temperature and pressure dependence is discussed.

In chapter 3 the Author presents entropic models of the glass transition, in particular the Adam-Gibbs model and its generalized form, the Avramov model as well as the density scaling of dynamics and entropy of glass forming liquids.

In chapter 4 experimental techniques used in this dissertation are briefly presented.

His own results presents the Author in chapter 5. First, (chapter 5.1, [1,3]) the relation between the transport properties (conductivity and viscosity) and configurational and excess entropy (calorimetric data taken from literature) was analyzed in the framework of the Adam-Gibbs model for three imidazolium based ILs: [BMIm][TFSI], [HMIm][TFSI] and [OMIm][TFSI], which differ by the length of the alkyl chain attached to the imidazolium ring (butyl, hexyl, octyl). It was shown that the viscosity of [BMIm][TFSI] in a broad T-range can be described by a single VFT function. Also a single set of VFT parameters was sufficient to describe the T-dependence of the conductivity of each of the three ILs. The glass transition temperature T_g slightly increased and fragility m_p slightly decreased with elongation of the alkyl side chain length. The temperature dependence of the excess entropy S_e and configurational entropy S_c was calculated using literature data. For all three ILs the excess entropy S_e was substantially higher than S_c and the relation $S_c \approx S_e$ was not valid. Two different methods were used to test the Adam-Gibbs model: (i) The S_c values calculated from the combination of the VFT equation and AG model were compared with values obtained from literature experimental thermodynamic data. It was shown that the AG model is not valid for description of viscosity of [BMIm][TFSI]. However, when S_c was replaced by S_e a satisfactory description was obtained. (ii) The Adam-Gibbs plot: $-\log_{10}\sigma_{dc}$ vs. $[S_c(T)T]^{-1}$ also failed to describe the conductivity data for all three ILs. Again a replacement of S_c by S_e resulted in a much better description of the data.

A correct description of the $\sigma_{dc}(T)$ data for all three ILS was also obtained when the generalized AG relation and the plot $-\log_{10}\sigma_{dc}$ vs. $[S_c^{\alpha}(T)T]^{-1}$ with $\alpha<1$ were used. A replacement of S_c by S_e in this relation also resulted in a correct description of $\sigma_{dc}(T)$ with higher values of α.

In the next step (chapter 5.2, [2,4]) the density scaling behavior of conductivity $\sigma_{dc}(T,P)$ was tested in a broad T,P range for several ILs using the BDS and PVT data. In this scaling a dynamic quantity (i.e. $\sigma_{dc}(T,P)$) is expressed as a function of a generalized variable $\Gamma=TV^{\gamma}$, where V is the specific volume and γ - the material dependent scaling exponent. When the exponent γ is chosen properly all the dynamic data measured at different T and P collapse on a single master curve. It was shown that such a master curve can be obtained for $\sigma_{dc}(T,P)$ of [BMIm][BETI] and [EMIM][DEP] ILs with constant γ_{σ} values of 2.85 and 2.15, respectively. The scaling exponents for different dynamical quantities (dc-conductivity, viscosity, diffusion) for several ILs (literature data) were compared and interpreted in terms of the steepness of the repulsive intermolecular potential.

Next, the density scaling was also applied to the entropy change $(S-S_r)$, S_r being the entropy at reference conditions ($T=T_g$, P=0.1 MPa). In this case the scaling exponent (Grüneisen parameter γ_G) can be calculated from thermodynamic data. A perfect scaling of entropy $(S-S_r)$ was obtained for [BMIm][BETI] and [EMIM][DEP] ILs with γ_G being a linear function of $(S-S_r)$. Using literature data it was also shown that the density scaling of entropy also works for fourteen ILs with different strength of interionic interactions. It was found that the sensitivity of γ_G to entropy decreases with increasing vdW and H-bonding interactions but increases with increasing electrostatic forces.

The studies of density scaling of entropy are very unique and important for understanding the physical nature of the glass transition.

In the last part of the thesis (chapter 5.2.4 and [4]) scaling of conductivity and entropy was tested for a polymerized IL – TPIL. BDS, PVT and TMDSC were used to measure the conductivity, volume and heat capacity of the sample. The scaling exponents γ_{σ} and γ_G were determined in the usual way. In contrast to the low molecular weight ILs the γ_{σ} was not constant but was changing with σ_{dc}, while γ_G was a linear function of $(S-S_r)$ as usual.

A brief summary of the results and potential directions of further research are given in Chapter 6.

The studies presented in this thesis belong to the leading themes in the field of ionic liquids.

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:

- Extensive test of ability of the Adam-Gibbs model to describe the T-dependence of dc-conductivity and viscosity of ILs in a broad T-range.
- Tests of validity of the density scaling for description of dc-conductivity and entropy of ILs in a broad T-P range.

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 better understanding of the relationship between the dynamics and thermodynamics of ILs and the nature of the glass transition in these materials.

The first introductory part of the PhD thesis (pages 1-28) which consists of introduction to the physics of ILs and the glass transition, 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 glass transition. This part will be very useful even for a reader less experience in the field and supplies the relevant literature (118 cited publications). Reading this part we can fully appreciate the Author's general knowledge in the field. The Results and discussion section is very consistent and well organized with a very well defined way o thinking leading to justified conclusions. The results obtained by the Author are clearly separated from literature data and compared with them, wherever possible. The main problem with this section is that, although all the discussed results have been published in four publications included in the thesis, there is no reference to them concerning figures, formulas, tables etc., which makes the combined reading of the commentary part and the original publications rather inconvenient.

In the course of his PhD studies Mr. Shinian Cheng became an expert in thermodynamic description of the dynamics of supercooled ILs and dynamic and thermodynamic methods used to obtain the data in a broad T-P range. As a graduate student he showed himself to be a very talented and hard working person with high theoretical and experimental skills able to solve independently scientific problems. He has also demonstrated a high ability to work with others.

The scientific value of the presented PhD thesis is very high. The author obtained very interesting, new and important results. All this led to important conclusions concerning the role of entropy in the description of relaxation dynamics of ILs. I have no doubt that the new very interesting results obtained by the Candidate essentially broaden our knowledge on the relations of dynamic and thermodynamic parameters of glass forming ILs.

I am fully convinced that the PhD thesis “The role of entropy in the description of relaxation dynamics of ionic liquids” by M. Sc. Shinian Cheng 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 public oral defense of the thesis.

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

Justification

The PhD thesis of M. Sc. Shinian Cheng consists of 4 multi-author publications published in high quality scientific journals. In all four publications Mr. Shinian Cheng is the first author and in the first three of them – one of the corresponding authors. Thus, his contribution to these publications is dominant. Additionally, he was a co-author of 10 publications not related to his PhD thesis (the first author in three of them) in leading scientific journals. He is a very active scientist involved in a very high quality scientific research. I am fully convinced that his PhD thesis deserves the distinction.

Poznań, August 18, 2021.

Prof. dr hab. Adam Patkowski