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Review of the doctoral thesis of Carolina Cruz Cardona, M.Sc. entitled

“Effect of Confinement on Ionic Liquids”

Ionic liquids are defined as salts in the liquid state at moderate temperatures (usually specified as below 100°C). These compounds are composed of organic and/or inorganic ions. The large structural diversity of ions, from inorganic to organic from chiral to achiral, including imidazolium, phosphonium, pyrrolidinium cations, and inorganic (e.g. nitrate, tetrafluoroborate, hexafluorophosphate) or organic (e.g. sulfacetamide, benzoate, alkylsulfates) anions gives rise to a number of unique physico-chemical properties of ionic liquids. These include nonvolatility, electrochemical and thermal stability. For these reasons the number of potential applications of ionic liquids is large and ever growing. The number of scientific papers published on ionic liquids has exponentially increased from several in the early 1990s to over 5000 in 2016. This demonstrates the importance of this scientific area.

In this context the topic of the submitted thesis has to be deemed as timely and of great potential interest. Not only is a good theoretical description of ionic liquids still lacking, but confinement effects generate on their own a host of interfacial phenomena even for “simple” liquids. Hence, when dealing with the confinement effects in ionic liquids, emergence of new important physics is almost guaranteed.

The Thesis consists of 9 chapters. In Chapter 4 the theoretical framework is presented. After a coarse-graining procedure the Author arrives at a grand potential mean-field functional comprising of several contributions, including the electrostatic, dispersion, external potential, entropy of mixing, excluded volume and the Legendre transform terms. Methods of solutions are presented in Chapter 5. Chapter 6 is devoted to the case of ionic liquid – solvent mixtures at a single charged wall while Chapter 7 presents the results of theoretical calculations for the ionic liquid – solvent mixture confined between two walls. Chapter 8 shows the results of molecular dynamics

calculations. They serve as an independent check of the theoretical predictions presented in the preceding chapters.

The scientific content of the Thesis has to be rated highly. In my opinion the most important findings of the Thesis include:

- formulation of a grand potential Landau-like functional for phase-separating mixtures of ionic liquid and solvent molecules;
- prediction of few different capacitance shapes including camel-like, bell-like and bird-like shapes and their connection to the thermodynamic state of the mixture, and wall ionophilicity;
- prediction of the capillary ionization transition for ionic liquid – solvent mixtures confined in slit-like pores and its dependence on the slit width and applied voltage. In particular it was interesting to observe reentrant behaviour for higher wall voltages.
- calculations of the energy stored in the systems. These results could be used to improve some of the energy storing devices.

The Author has not, however, avoided some shortcomings that require further clarification.

- When considering ionic liquid – solvent mixtures at a single wall, I could not find any information about the wetting state of the wall. While there is a measure of the wall-fluids attractive interactions (relative to the fluid-fluid interactions) one has to wonder what about the contact angle, wetting point etc. This question becomes even more important after the Author mentions wetting transition already in the Introduction on page 1.
- In Chapter 7 the Author considers capillary ionization in non-polarized and polarized slit-like pores. We enjoy nice figures with well described bulk phase behaviour, predictions of the Kelvin equation and the theoretical results. However, it is well-known that in simple fluids there is a shift in the critical point due to confinement [M.E. Fisher and H. Nakanishi, *J. Chem. Phys.* **75**, 5857 (1981)]. The bulk critical point is marked with a big black dot for example in Fig.7.1. But what happens with the critical point under confinement? Likewise, for the systems with oppositely charged walls, it is again well known that for simple fluids the critical temperature will tend towards the wetting temperature of a single wall while above



that temperature (but below the bulk critical temperature) the system is characterized by a single soft mode phase. Again the Reader is left wondering what would happen here?

- In Chapter 8 a comparison with molecular dynamics simulations was carried out. A way of mapping the simulational parameters onto the ones used in the theoretical calculations was presented. It's a pity that the simulations were done for a very simple "toy" model. It would be quite momentous if we were able to compare the theoretical predictions with the simulational results of an all-atom model of some selected ionic liquid – solvent mixtures but I do realize that the computational effort could be substantial. However, I am a little surprised that in order to estimate the critical point of the simulational systems the Author used Ornstein-Zernike integral equation framework within the hypernetted chain approximation. We all know limitations of the hypernetted chain approximation, and in this day and age there exists a number of viable ways of estimating the critical parameters from the actual simulations. I agree that, as mentioned by the Author, the full grand canonical simulation is not a feasible option here, but using block distribution analysis [cf. *J. Chem. Phys.* **136**, 204102 (2012), *Entropy* **20**, 222 (2018)] it should be possible to determine the critical properties using NVT molecular dynamics simulations. It is especially important if one wishes to estimate accurate critical parameters including finite size effects.
- In Chapter 9, in concluding remarks the Author provides a discussion of the implications of the approximations used in the proposed functional. It is important since it demonstrates how well the Author understands the subject of her investigations. While the local density approximation is mentioned in the text, another important approximation is not. It is the mean field character of the functional. It would be nice to know which predictions should remained unchanged and which ones are expected to be altered if the fluctuations are included in a proper manner. This would additionally underline the robustness of the main findings of the Thesis.
- On page 34 the Author mentions a method of numerical solution (bvp4c from MATLAB). In my opinion it would be much better if the actual numerical method was described as not everyone has access to MATLAB. Its eventual implementation may differ from one numerical library to another.

The editorial side of the Thesis is excellent with cover artwork worthy of a professional publishing house. It is a real pleasure to read clearly written content and look at neatly prepared figures. The only downside for me is relative untidiness with accurate referencing scheme (cf. Refs. 2, 147, 148, 150, and few others).

Summing up, despite some critical remarks the overall quality of the Thesis is, in my opinion, very high. The Author has formulated and solved an original scientific problem. The scientific content of the Thesis has been already published in three papers. **I conclude that the requirements of the Polish legal act about academic degrees from 14 March 2003 (Dz. U. Nr 65/2003 poz. 595 with later amendments) are fulfilled and that Carolina Cruz Cardona should be allowed to the next stage of the doctorate degree procedure.**

In this Thesis the incompressibility constraint was adopted. In real mixtures both the ionic liquid and solvent densities are independent variables. The consequence of this fact is that the full bulk phase diagrams of ionic liquid – solvent mixtures will be much richer [according to the classification of van Konynenburg and Scott, *Philos. Trans. R. Soc. London Ser. A* **298**, 495 (1980)], with potential multicritical points, cf. *AIChE Journal* **52**, 3952 (2006), *AIChE Journal* **55**, 486 (2009), *J. Supercrit. Fluid* **55**, 825 (2010). For this reason I expect continuation of the scientific work started in this Thesis with many interesting findings to come in the near future. This is in addition to the fact the scientific content of the Thesis has been already published in three papers following by the next two pending manuscripts. **Considering the above facts, as well as excellent editorial work I recommend the Thesis to be awarded as an outstanding Thesis by the Council of the Institute.**

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