RFEREE REPORT

From Prof. DSc Peter Atanassov Kralchevsky, Sofia University
Fellow of the Bulgarian Academy of Sciences
Chair of the Scientific Jury for the PhD thesis defense appointed with
Order № RD38-144/20.03.2020 of the Rector of Sofia University "St. Kliment Ohridski"
PhD Thesis for the Educational and Scientific Degree "Doctor of Philosophy"
Professional field: 4.2. Chemical Sciences (Physical Chemistry – Macrokinetics)
Author of the Thesis: **Diana Peychova Cholakova**, regular PhD student in
Dept. «Chemical and Pharmaceutical Engineering» (CPE),
Faculty of Chemistry & Pharmacy (FCP), Sofia University (SU)

Title of the PhD Thesis:
"*Spontaneous deformation of emulsion drops undergoing phase transitions*"

Brief biographical data for the PhD candidate. Diana Peychova Cholakova was born in 1993 г. in Sofia. In 2012, she graduated the National High School of Natural and Mathematical Sciences "Academician L. Chakalov" with excellent marks. During the High School period, she took part in several national and international mathematical Olympiads, and won three bronze medals from international mathematical Olympiads. In 2016, she graduated the Bachelor Program "Chemical Engineering and Advanced Materials" of the Faculty of Chemistry & Pharmacy, Sofia University. In March 2018, she graduated the Master Program "Disperse Systems in Chemical Technologies" in the same faculty. Since July 2018, she has been PhD student in the Dept. "Chemical and Pharmaceutical Engineering", under the supervision of Prof. DSc. Nikolai Denkov, Corresponding Member of the Bulgarian Academy of Sciences. During her student period, Diana Cholakova won several prestigious awards, as follows:

 Award "The best student of 2016" of the Sofia University "St. Kliment Ohridski" – First position in the category "Natural Sciences", and second position in the general ranking.
 Aquachim Award for the best PhD Thesis defended during the 2016-2017 academic year.
 The great Award "The best student of 2017" of the Sofia University "St. Kliment Ohridski".
 Enzo Ferroni Award for best oral presentation by young scientist, 33rd Conference of the European Colloid & Interface Society, Leuven, Belgium, September 2019.

Scientific publications. Diana Cholakova is co-author of 12 papers in reputed international journals, including *Nature*; *Nature Communications*; *Adv. Colloid Interface Sci.*; *Langmuir*; *Phys. Rev. Research*; *Curr. Opin. Colloid Interface Sci*. и *Soft Matter*. 74 independent citations of these publications have been noticed. Three of these papers

are included in her PhD Thesis. Two of them were published in 2016 in the journals *Adv. Colloid Interface Sci*. (IF = 8.243) and *Langmuir* (IF = 3.683), and the third one was published in 2019 in *Langmuir* again. 17 independent citations have been noticed of these recent publications.

Reporting at scientific conferences. The results included in the PhD thesis were reported by 14 presentations at scientific events. Among them, six oral presentations and two posters were presented personally by the PhD candidate.

Parameters of the PhD thesis. The volume of the thesis is 128 pages, including 54 figures, 9 tables, 21 equations and a list with 142 references.

Theme of the PhD thesis. The thesis belongs to the series of studies by Prof. Nikolai Denkov and coauthors on the shape transformations of emulsion drops from liquid paraffins, which are subjected to cooling and freezing. These changes in the shape have been explained with the formation of rotator phases in the vicinity of the drop surface. In the thesis, the factors that control the process of spontaneous deformation upon cooling of dispersed droplets from alkanes and other non-polar hydrocarbons. By experiments with differential scanning calorimetry and X-ray scattering, the fraction of the ordered molecules in the drops, as well as the structure of the ordered array corresponding to rotator phase is determined. By means of the developed theoretical model the experimental data are interpreted and the thickness of the layer from rotator phase is estimated.

The thesis is written very clearly in good Bulgarian language and is illustrated with many figures and tables, which give both qualitative and quantitative information for the investigated interesting phenomena. The conclusions are supported by experimental data obtained by several appropriate methods. Two of them are available (and the data have been obtained by the PhD student) in foreign research centers.

I have two questions to the PhD candidate:

1. In Fig. 37, it is shown that 10 μm hexadecane drops freeze at 6 °C. However, it is known that the melting temperature of hexadecane is 18 °C. To explain this difference, two hypotheses could be proposed:

A) The emulsion drop s small; the probability for formation of a critical nucleus in the drop is also small so that the crystallization occurs at a lower temperature – in super-cooled hexadecane.

B) The heat transport across the liquid paraffin is slow enough, so that the temperature in the drop center could be ca. 18 °C, whereas the outer temperature is 6 °C.

Which of the two hypotheses, A or B, is closer to reality?

2. Could you present arguments in favor of the interpretation of the observed phenomena via the formation of rotator phases, in comparison with the alternative interpretation without rotator phases proposed by Guttman et al., Ref. [126] и [127]?

Conclusion: The thesis represents a systematic experimental study on a very interesting phenomenon. Effects of various factors on different systems alkane/surfactant are investigated. The data are systematized and quantitatively characterized in the framework of developed theoretical model. Regularities in the systems' behavior are established and adequate physicochemical interpretation is given. The three papers on the thesis have been published in journals with high impact factor and have already attracted the attention of the international scientific society, which is evidenced by the found 17 citations of these recent publications. The thesis completely satisfies the criteria of the Faculty of Chemistry and Pharmacy of Sofia University for the PhD degree. I am convinced that the candidate deserves the degree and will vote the Educational and Scientific degree "Doctor of Philosophy" to be given to MSc Diana Peychova Cholakova.

Date: 7th May 2020

Chair of the jury:

Prof. DSc Peter A. Kralchevsky