EVALUATION REPORT

on THESIS submitted
for the acquisition of educational and scientific degree “Doctor of Philosophy” (PhD)
Specialty: 4.2 Chemical Sciences (Physical Chemistry – Macrokinetics)

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Title: “ Spontaneous deformations of emulsion drops undergoing phase transitions”

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The PhD Thesis of Diana Cholakova is focused on the design and investigation of the behavior of oil-in-water emulsions. This topic is closely related to the contemporary approach to initiate new products and innovative applications which are linked directly to the improvement of man’s life conditions: nanotechnologies, biotechnologies, food, pharmaceutical and cosmetic industries. The development of reliable methodologies for control over the structural characteristics of emulsion droplets and the gain of systematic knowledge about the stabilization mechanisms in these systems present a modern trend in the field of fundamental and applied research.

The major goal of the PhD Thesis is to clarify the physicochemical factors which determine the spontaneous deformation of the emulsion drops during cooling of the system. The key idea is that with the appropriate selection of the composition in the system and the conditions under which cooling is carried out, changes in the shape of the drops might be controlled. The concept is based on experimental evidences known from previous research publications, namely: in the transition process between isotropic liquid and ordered crystalline state intermediate rotator phases (plastic crystals, highly ordered smectics) might appear. In the present Thesis the idea is developed in detail via focused design of model experiments; a well-substantiated quantitative model for the interpretation of the experimental data is proposed so that to extract and outline important characteristics of the formed rotator phases in different emulsion systems.

The PhD Thesis is structured into Introduction and four chapters. Diana Cholakova is well acquainted with the scientific background of the research field. The cited references are 142. The Introduction clearly outlines the previous studies, basic concepts are consistently introduced, important properties of the emulsions are extensively commented, the peculiarities of alkane freezing are systematically described, including the possibilities for the onset of rotator phases. Special attention is paid to the previously known data about the evolutionary cooling scheme and the conditions for obtaining emulsion drops with non-spherical shapes. An in-depth analysis of the basic concepts and the model assumptions is presented regarding the interpretation of results from previous studies and the relationships to spontaneous droplet deformations in the process of controlled cooling. It is important to note that the doctoral student was involved in some of these earlier research studies as an undergraduate at FCP-SU (see for example № 1-4 from the list of the additional publications: *Nature*, 2015, 528, 392-395; *Phys. Rev. Lett.*, 2017, 118, 088001-1 –

088001-5; *Nat. Commun*., 2017, 8, 15012; *Langm*uir, 2017, 33, 12155-12170). This fact evidences a continuous and profound preliminary qualification in this area of the research. The Introduction ends with the outline of the Thesis goal and the formulation of the basic research tasks. Chapter 2 contains data about the materials and the applied research instrumentation. Excellent impression is left by the clear and comprehensive arguments related to the choice of the investigated formulations, as well as by the appropriateness analysis for the selected experimental methods and research procedures.

The PhD research accomplishments of Diana Cholakova are presented in Chapters 3-5. The experimental data are abundantly detailed and systematic assessment of the obtained results is properly presented. The factors and sequential stages which influence the spontaneous deformation processes in cooling of the emulsion drops from alkanes and other well-chosen non-polar compounds (for example 1-alkenes, n-alcohols) are consistently demarcated in Chapter 3. The role of the applied surfactants is clarified, incl. the importance of the size and the structural peculiarities of their hydrophobic and hydrophilic portions; a classification of the systems alkane-surfactant (in 4 groups) is presented, regarding their effect on the deformation of hexadecane droplets. It is established that surfactants change the starting temperature of deformation, affect the final shape of the drops, determine the onset of specific structures (rod-like particles and long asperities for in case of prismatic and ellipsoidal platelets). In Chapter 4 the mechanism of the evolution of droplet deformation upon cooling is discussed and the structural changes are related to the onset of rotator phases. Through direct experiments (DSC and SAXS) the fraction of the ordered molecules is determined, as well as the type of the ordered plastic rotator phase. In Chapter 5 a theoretical interpretation of the results is performed which allows to estimate the thickness of the surface plastic rotator phase. The Thesis ends with a list of references and an overview of the main scientific contributions of the performed research; additional activities and other publications of Diana Cholakova are also mentioned; scientific indicators related to the performed PhD studies are included.

The most important research achievements of the Thesis are:

1. The key factors for reaching the final stages in the universal evolutionary sequence of droplet deformations have been identified, namely (a) smaller initial size of the droplets; (b) presence of surfactants having lengths of the hydrophobic tails similar or slightly larger than the molecules of the oil phase; (c) lower cooling rates. These are evidenced as general tendencies for oil-in-water emulsions in which the oil phase is composed of long saturated alkyl chains.

2. It is established that upon controlled cooling of oil-in-water emulsions the deformation commencement in the disperse phase could be related to freezing of the surfactant adsorption layer on the drop surface. This process initiates ordering of the adjacent layers of nonpolar hydrophobic molecules into a phase demonstrating structural characteristics similar to a crystalline phase. The curvature of the droplet's surface and the adjacent subsurface initiates impaired arrangement of molecules in its volume resulting in further accumulation of defects in the internal molecular layers, where the arrangement exhibits properties of the less-ordered rotator phase.

3. A theoretical interpretation of the experimental data is proposed for the assessment of the rotator layer thickness at the droplet's surface. The estimation shows that the rotator layer thickness may vary in-between a few lengths of alkane molecules upto 24 ± 6 stacked monolayers depending on the specific emulsion formulation. A hypothesis is advanced about the structural peculiarities of

the rotator phases as being similar to the configuration in solid crystals. Most probably this initiates enhanced interactions between the layers in the plastic phase and results in significant resistance to shearing of the neighboring layers. The bending elasticity constant of the layer runs as a cubic function of itsr thickness and the properties of these layers might be adequately described by Kirchhoff–Love model for thin elastic shells.

The studies reported in the PhD Thesis hold a high degree of novelty and originality. They represent a systematic and carefully conducted experimental investigation combined with very well-substantiated theoretical modelling of the physico-chemical factors and mechanisms which govern the spontaneous deformations in emulsion droplets upon cooling. The research achievements are summarized in four major points. I accept these accomplishments and consider them as representation of well-formulated experimental and model theoretical approaches for design and investigation of this type of oil-in-water emulsions. The results obtained constitute a new scheme for the acquisition of data related to existing research problems and hypotheses; they suggest an important databank for further fundamental studies and innovative industrial applications.

As a whole, the Thesis content is properly organized, with clear definition of the scientific challenge, the research goals, the implemented experimental and theoretical approaches. The obtained results are very well-formulated and convincingly analyzed in due details. No doubt, they add essential new knowledge about the investigated processes and help in the development of better quantitative interpretation and effective control over the parameters of emulsion systems.

The studies are included in three papers published in two high-ranked peer-reviewed scientific journals: *Advances in Colloid Interface Science*, 2016, 235, 90-107 (IF= 8.243, Q1) и *Langmuir* 2016, 32, 7985-7991; 2019, 35, 5484-5495 (IF= 3.683, Q1). The PhD Student is first author in two and a second author in one of the papers. These publications have been cited 17 times by now. The research outcomes have been reported at international and national scientific events as 11 oral presentations (6 of them delivered by the applicant) and 3 posters. It should be mentioned that the oral report at 33rd European Colloids and Interfaces Society Conference 9-13.09.2019 in Leuven, Belgium was awarded as "Best oral presentation delivered by a young researcher", a prize given by Enzo Ferroni Foundation. A poster at the International Conference in Homerton College, Cambridge, UK, 3-6.04.2016 got also a distinction as a best poster presentation. These scientific indicators provide plain evidences that the results reported in the Thesis may, to a considerable degree, be viewed as personal achievements of the PhD student.

In addition, Diana Cholakova is a co-author of nine other scientific papers; in three of them being also the first author: 1 in *Nature* (2015), 1 in *Phys. Rev. Lett*. (2017), 1 in *Nat. Commun*. (2017), 2 in *Langmuir* (2017, first author of one of them), 1 in *Adv. Colloid Interface Sci.* (2019, first author), 1 in *Phys. Rev. Research* (2019), 1 in *Curr. Opin. Colloid Interface Sci*. (2019) and 1 in *Soft Matter*, (2020, first author). These publications have been cited 56 times. The provided Thesis documents, as well as the excellent presentation at the pre-defense, confirm the opinion that the applicant is a highly educated, successful and talented young researcher.

The research has been performed in Department of Chemical and Pharmaceutical Engineering, Faculty of Chemistry and Pharmacy, Sofia University "St. Kliment Ohridski". According to the attached report on the fulfilment of the minimum national requirements linked to Art. 2b of the Act on Development of the Academic Staff in the Republic of Bulgaria for Specialty: 4.2 Chemical Sciences (Physical Chemistry – Macrokinetics), all necessary conditions for the acquisition of the requested scientific degree (PhD) are fulfilled (50 points for Group A, 75 points for Group G). The Thesis Summary is composed according the rules and reflects properly the research content and the scientific achievements of the performed PhD investigation.

Based on the above I am convinced that the proposed PhD Thesis completely fulfils and exceeds in quality and quantity all the requirements as stated in the Act on Development of the Academic Staff in the Republic of Bulgaria, the Rules for its implementation, and the Specific criteria for the acquisition of the requested scientific degree in Sofia University "St. Kliment Ohridski". I strongly recommend to the Honourable Scientific Jury to award the doctoral student Diana Peychova Cholakova the educational and scientific degree "Doctor of Philosophy (PhD)" in the Speciality 4.2 Chemical Sciences (Physical Chemistry – Macrokinetics).

Evaluator:

May 10, 2020, Sofia (Elena Mileva, Professor, DSc)