REVIEW

of a dissertation paper to acquire an educational and scientific degree “Doctor of Philosophy” in Professional Field 4.2 Chemical sciences (Physical chemistry – Macrokinetics)

Author of the dissertation paper: Diana Peychova Cholakova, a regular PhD student at the Department of Chemical and Pharmaceutical Engineering – Faculty of Chemistry and Pharmacy, Sofia University ‘St. Kliment Ohridsky’

Title of the dissertation paper: ‘*Spontaneous Deformations of Emulsion Drops Undergoing Phase Transitions’*

Supervisor: Prof. Nikolai D. Denkov, DSc

Reviewer: Assoc. Prof. Khristo Khristov, PhD, Institute of Physical Chemistry, BAS

Systematic studies of processes and factors defining alkane emulsion droplets shape in surfactant solutions at cooling were initiated about five years ago at the Department of Chemical and Pharmaceutical Engineering and under the supervision of Prof. Nikolai Denkov. Part of the studies focused on clarifying self-emulsification processes running at cooling and heating of alkane droplets, stabilized by a suitable surfactant. It is a well-known fact that systems strive to a minimum of free energy which is the reason for the spherical shape of droplets in a typical emulsion. Obtaining droplets of a different than spherical shape requires additional energy. The dissertation presented focuses on elucidating the very mechanisms and factors regulating the shape evolution of spherical emulsion droplets formed by alkane and other suitable substances at cooling. A confirmation of the fundamental and practical application of the dissertation studies are the papers published in the scientific field pertinent to the dissertation topic in the last five years, being cited over 80 times by other authors (as per Scopus data).

The dissertation comprises 128 pages, 54 figures, 9 tables and 21 equations. Referenced are 142 sources, the predominant part being published in the last 10 years. The dissertation is based on three papers published in renowned scientific journals, namely: two in 2016, the first in *Adv. Colloid Interface Sci.*, impact factor (IF) 8.243, Q1, the second – in *Langmuir*, IF 3.68, Q1, and one in 2019, in *Langmuir*, IF 3.68, Q1. To date a total of 17 citations on these papers have been found (8 for the first paper; 7 for the second paper; 2 for the third). Results included in the dissertation have been reported at 14 scientific forums with 11 oral and 3 poster contributions. PhD student Cholakova has presented 6 of the oral interventions. The one delivered at the *33rd European Colloids and Interfaces Society Conference* in Leuven, Belgium, 9-13 Sept 2019, was awarded **Enzo Ferroni Foundation's best oral presentation by a young researcher.** The poster presented at *Solutions in the Spring*, in Homerton College, Cambridge, the UK, 3-6 April 2016, also received an **award for the best scientific poster**.

The dissertation paper contains five chapters: Introduction; Materials and Experimental Methods; Experimental Results – described in the third and fourth chapters, and Theoretical Interpretation of the results obtained – in the fifth chapter. Main contributions are summarised at the end of the dissertation, along with References and List of Acronyms used.

The Introduction gives a clear rendition of principal concepts, processes, mechanisms and factors, together with published experimental results and theoretical notions relevant to the dissertation topic, namely, deformation of emulsion droplets in surfactant solutions. Particular attention is paid to previous studies in the field as well as to properties of rotator phases formed in solution volume and surface at alkanes or alkane mixtures cooling. It is evident that PhD student Cholakova has an excellent grasp of the contemporary knowledge in this relatively new scientific area and is capable of applying this knowledge in her dissertation studies in a creative manner.

The second chapter deals with the properties of materials used such as surfactants, alkanes, oil phases, etc. Sample preparation procedures and experimental methods employed are also described. The main experimental results referring to clarification of mechanisms of emulsion droplet deformation are obtained using differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS).

The most substantial results of the experimental studies regarding the role of various factors responsible for the processes of spontaneous emulsion droplet deformation at cooling, described in Chapter Three, are: a) emulsion droplet deformations at cooling are observed in both alkanes and other non-polar substances forming intermediate rotator (plastic) phases at cooling; b) a general evolution sequence in the transition from one shape to the next is found and established to depend on the particular alkane+surfactant system; c) in droplets of smaller size (less than 16 microns) and at lower cooling rate, deformation values before freezing are larger; d) the process of spontaneous droplet deformation depends on the type of surfactants in the system. These targeted studies produced an extensive volume of experimental data regarding the effect of various factors and served as basis for explaining the mechanisms of non-spherical droplet formation. Systematically collected interfacial tension, thermal and X-ray scanning data, treated in Chapter Four, allowed to establish the formation of intermediate rotator phases at the emulsion droplet surface that led to the droplet deformation observed at cooling.

The last fifth chapter offers the theoretical models developed to provide a qualitative explanation of the experimental data obtained with the aim of determine rotator phase thickness at the surface of deformed droplets. It is demonstrated that deformations of emulsion droplet shape at cooling are due to formation of rotator phase multilayers located at droplet surface. The thickness of these multilayers varies from 5 to 180 nanometres which corresponds to 2 up to 80 layers of arranged molecules. It is proven that droplet deformation is unlikely to be attributed to a frozen layer at the surface because the system interfacial energy has to be lower in two or more orders than the interfacial tension value measured.

I believe that experimental results obtained are undisputable. The PhD student has applied the experimental methods in a consistent and deliberate manner in order to attain the purpose and objectives of the dissertation. Data obtained by one of the methods are confirmed and/or supplemented by the other methods employed. The theoretical analysis stands high scientifically and its outcomes hold high scientific merit.

The dissertation is very well arranged and presented, and there is no doubt in my mind that to a major extent, the scientific contributions can be assigned to PhD student Cholakova.

Dissertation Summary reflects correctly the main applications and scientific contributions of the studies carried out.

The main scientific contributions (four) are defined precisely: the first two reflect new experimental results obtained while the second two provide a theoretical analysis of the experimental data accumulated in the course of the dissertation studies. Dissertation contributions are of both fundamental and applicable nature.

I have no remarks on the dissertation paper presented for reviewing. I have not detected any mistakes or typos worth commenting.

Conclusion

In view of the significance of scientific outcomes achieved, I consider that this dissertation paper exceeds substantially the requirements to grant an educational and scientific degree "Doctor of Philosophy". I recommend to my honourable colleagues – members of the Scientific Jury – to award Diana Peychova Cholakova the educational and scientific degree "Doctor of Philosophy" in Professional Field 4.2 Chemical sciences (Physical chemistry – Macrokinetics).

10 May 2020 Reviewer:

(Assoc. Prof. Khristo Khristov, PhD)