

## OPINION

by Assoc. Prof. Dr. Velyana Georgieva Georgieva,

Head of the Department of Chemistry

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Regarding the quality of doctoral thesis in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field **4.2 Chemical Sciences**, scientific specialty

***Inorganic chemistry***

**Author:** Dencho Ivanov Mihov

**Title:** Experimental and theoretical studies of selenate systems

**Scientific supervisor:** Assoc. Prof. Dr. Rumiana Yankova-Avramova, "Prof. Dr Assen Zlatarov" University - Burgas

### 1. General presentation of the procedure

The set of documents presented by the PhD student Dencho Mihov in paper and electronic form are in accordance with the requirements of the Law on the Development of Academic Staff of the Republic of Bulgaria, as well as with Procedure for Acquisition of Academic Degrees and Habilitation Procedure at "Prof. Dr Assen Zlatarov" University.

Dencho Mihov was enrolled as a regular PhD student at the Department of Chemistry on 15.02.2021 and was discharged with the right to defend on 20.10.2022.

### 2. Biographical data

Dencho Mihov graduated in 1988 as a chemical engineer in the specialty "Chemical Technologies", Master's degree at the then Higher Institute of Chemical Technology "Prof. Dr. Asen Zlatarov"- Burgas. After his graduation he started working as an assistant at the same university, and within his 10 years of experience he passed through the academic positions of "senior assistant" and "chief assistant". Since 1999 he has held managerial position in a company and in the publishing house "Libra Scorp" – Burgas.

### 3. Topicality of research area

One of the main problems in the chemical industry and in particular the production of inorganic substances is the determination of the concentration range of existence and purity of a given salt in a multicomponent system. In this regard, the study of multicomponent systems containing alkali selenates and selenates of divalent metals - mainly of the first order of transition metals in aqueous media, I define as the current topic of this dissertation, aimed at the synthesis of new compounds with potential applications in medicine, engineering and agriculture, as well as establishing the possibility of predicting the type of solubility diagrams.

### 4. Characteristics and evaluation of the PhD thesis

The aim of the thesis is precisely defined in the introduction and is related to the thermodynamic study of phase equilibria in metal selenate systems in order to obtain new salts. Achievement of the goal is linked to specific research tasks and obtaining real results. The research methods are outlined, including experimental and theoretical approaches.

The PhD thesis is 144 pages long, in which the results are illustrated with 30 tables and 18 figures. The attached bibliography includes 199 references from 1923 to 2021, of which only 10 are from the last 10 years. The table of contents is structured in the following sections Introduction; Literature review; Development of thermodynamic studies of mixed solutions of strong electrolytes; Experimental data from equilibrium studies in ternary water-salt selenate systems; Experimental data from the isopiestic study of selenate systems; Heat capacities, enthalpy, entropy and thermochemical potential of selenate solid phases; Interpretation of solubility diagrams of selenate systems at 25°C; References; Scientific contributions; Scientific publications on the subject; Participation in scientific forum.

The literature review presents in detail the triple selenate systems studied so far and the preparation of their double salts. From the detailed literature review, it is found that only systems involving lithium, sodium, cesium and rubidium selenates have been poorly studied and there is a lack of studies on the structure of these compounds except for the alkali selenates. No studies were found on the determination of activity coefficients in binary and ternary systems of selenates.

In the section "Development of thermodynamic studies of mixed solutions of strong electrolytes", various methods for calculating activity coefficients and osmotic coefficients of electrolytes are outlined, with emphasis on the Pitzer method applied to describe the thermodynamic properties of solutions of binary and multicomponent systems. I believe that this section can be added to the literature review as it describes theoretical methods for calculating thermodynamic functions of state and determining electrochemical quantities.

In the section "Experimental data from equilibrium studies in ternary water-salt selenate systems", the methodologies for the preparation of the initial selenates of the alkali metals and of some divalent metals, the methodologies for the determination of the metal and selenate ion contents of the solutions, and the compositions of the existing equilibrium phases of 16 ternary systems at 25°C are presented. For each of the systems, the solubility isotherm was constructed by the *Rozeboom* method, the *Schreinemakers* method was applied to determine the solid phase compositions, the liquid and wetted solid phase compositions are tabulated. It is found that the following four of the 16 investigated triple systems of simple eutonic type are  $\text{Li}_2\text{SeO}_4 - \text{MgSeO}_4 - \text{H}_2\text{O}$ ,  $\text{Li}_2\text{SeO}_4 - \text{CoSeO}_4 - \text{H}_2\text{O}$ ,  $\text{Li}_2\text{SeO}_4 - \text{NiSeO}_4 - \text{H}_2\text{O}$  and  $\text{Na}_2\text{SeO}_4 - \text{NiSeO}_4 - \text{H}_2\text{O}$  at 25°C. For the remaining 12 ternary systems, double salts were obtained and their crystallization existence fields were delineated. I must emphasize that the construction of each solubility isotherm required an extraordinary amount of experimental and technical work, and I commend the PhD student for the effort and work put in.

In the next section, the relationship between activity and molality of a component in binary solutions of alkali selenates is investigated and the *Pitzer* method is applied to calculate activity coefficients in binary selenate systems. A computer program has been developed to calculate the activity coefficients of the studied binary systems.

In the section "Heat capacities, enthalpy, entropy and thermochemical potential of selenate solid phases", experiments were carried out to prove the water content of crystal hydrates and anhydrous selenates and their double salts were obtained. On the basis of the calorimetric investigations carried out, the temperature dependence of the molar heat capacities of the compounds investigated has been deduced and the thermodynamic functions of the alkaline selenates have been determined.

The application of different mathematical approaches in the calculations of various thermodynamic functions and electrochemical quantities is noteworthy, which is indicative of the



multidisciplinary nature of the conducted research and the serious theoretical knowledge of the PhD student. The interpretation and analysis of the obtained results are made with thorough comprehensiveness. A correlation between the calculated physicochemical characteristics of the investigated systems and the methods used has been sought, which gives grounds for the originality of the conclusions drawn.

The dissertation work contains scientific and applied results that build on the known knowledge in the field of inorganic chemistry and in particular physicochemistry and meets all the requirements of the Law on the Development of Academic Staff in the Republic of Bulgaria.

#### **5. Assessment of publications and personal contribution of the PhD student**

The required indicators of the candidate, according to the Law on the Development of Academic Staff in the Republic of Bulgaria and Procedure for Acquisition of Academic Degrees and Habilitation Procedure at "Prof. Dr Assen Zlatarov" University are as follows:

##### **Group of indicators A:**

Indicator A1 PhD thesis – prepared thesis on „Experimental and theoretical studies of selenate system“ in professional field 4.2 Chemical Sciences – **50 points**;

##### **Group Γ indicators**

Indicator *Γ7 Scientific publications, referenced and indexed in databases Web of Science and Scopus* – 3 publications are attached, respectively in quartiles: **Q2** – 1 published in *Journal of Molecular Structure* in 2022; **Q3** - 1 published in *Chemical Data Collections* in 2021 and 1 published in indexed and refereed journal *Monatshefte fur Chemie* in 1993 - **35 points**;

**Total for all groups indicators 85 points**

It is evident from the submitted reference that the candidate exceeds the minimum national requirements under Law on the Development of Academic Staff in the Republic of Bulgaria and Procedure for Acquisition of Academic Degrees and Habilitation Procedure at "Prof. Dr Assen Zlatarov" University. The personal contribution of the candidate can be judged by the position in the author collective of a publication. In the first of the declared articles he is on the second position, in the second - on the first, and in the third - on the third.

The PhD student has reported part of the obtained results at 3 scientific forums with a total of 4 participations - 1 in the National Congress of Medicine "Challenges to Medical Science and Practice in the XXI Century", 2022 and two conferences with international participation - 1 scientific report in the XXXI International Scientific Conference 60 years Union of Scientists - Stara Zagora, 2021 and 2 papers in the Conference with international participation "Oil and Chemistry '90", Burgas, 1990.

In addition to the publications presented in the report, the candidate has 7 more articles published in refereed and indexed journals. The high productivity and importance of the candidate's publications can be judged by the total number of citations - 53 and Hirsch index h - 5.

#### **6. Abstract of a dissertation**

The proposed abstract outlines the main content of the doctoral thesis and gives a clear picture of the done work by the PhD student. I fully accept the contributions made by the PhD student concerning the enrichment of knowledge on the preparation of various selenates and their double

salts, as well as on the determination of their thermodynamic functions and electrochemical characteristics with potential application in medicine, engineering and electrochemistry.

## CONCLUSION

I have known PhD student Dencho Mihov since his enrolment at the "Prof. Dr. Asen Zlatarov" University and I have observed his purposefulness, diligence and a strong sense of responsibility and consistency in his work. The overall presentation and performance of the present study strongly confirms the opinion of demonstrating qualities and skills for independent scientific research.

In accordance with the enclosed scientific publications, the obtained results, their precise interpretation and the made scientific and applied contributions, I give a positive evaluation to the dissertation work on "Experimental and theoretical studies of selenate systems". I propose the Honourable Scientific Jury to grant the educational and scientific degree "Doctor" to Eng. Dencho Ivanov Mihov in the field of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2 Chemical Sciences, scientific specialty Inorganic Chemistry.

15.12.2022 г.

Member of the Scientific Jury:

Подпис заличен  
Чл.2 от ЗЗЛД

(Assoc. Prof. Dr. Velyana Georgieva)