REVIEW

by *Assoc. Prof. Svetlana Dimitrova Zheleva, PhD, "Prof. D-r Asen Zlatarov" University of Burgas*

of dissertation for the award of the educational and scientific degree **"PhD"**

Area of higher education **4. Natural Sciences, Mathematics and Informatics**

Professional field **4.2. Chemical sciences, Doctoral programme "Inorganic chemistry"**

Author of the dissertation: **Eng. Dencho Ivanov Mihov** - regular PhD student at the Department of Chemistry, "Prof. D-r Asen Zlatarov University" of Burgas

Academic advisor: **Assoc. Prof. Rumyana Yankova, PhD**

Dissertation: **"Experimental and theoretical studies of selenate systems"**

Reason: member of the scientific jury in the dissertation defense procedure for obtaining the PhD degree, according to the Order No. УД-289/26.10.2022 of the Rector of "Prof. D-r Asen Zlatarov" University of Burgas

1. Brief biographical data

Dencho Ivanov Mihov was graduated from VHTI "Prof. D-r Asen Zlatarov" in 1988 and awarded a Master's degree with a professional qualification "Chemical Engineer". Immediately after his graduation he was started working at VHTI "Prof. Dr. Asen Zlatarov" as an assistant in the Department of Inorganic Chemistry and during 10 years he was taught and developed research activities, rising to the academic position of "Chief Assistant". In 1999, he left the higher education structure and started working as a manager in the Employment and Structural Development Department in Aytos, where he was responsible for organizing and providing temporary employment. Since 2002, he has been the manager of the Libra Scorp Publishing House and is engaged in publishing books: fiction, scientific literature (textbooks, teaching aids for students, scientific monographs) and popular scientific literature.

In February 2021 Dencho Mihov is enrolled in the full-time PhD program "Inorganic Chemistry" at the Department of Chemistry of the "Prof. Dr. Asen Zlatarov" University of Burgas and within less than 2 years he prepared and presented his dissertation for defense. Undoubtedly, the academic experience that the candidate has, as well as his long professional experience as a publisher, contribute to the good organization of his work and his timely preparation for the doctoral program.

2. Comments on the dissertation

The dissertation of Dencho Mihov represents an actual scientific research on the study of selenate systems of monovalent and divalent metals, which are of increasing importance in practice – they are used as an additive in electrolytic extraction of manganese or in electrolytic boron

coatings, in medicine for the study of their inhibitory effect on tumors, in agriculture as insecticides, etc. The study of the processes of formation of mixed crystals and double salts and the mastery of the fundamental patterns to which they obey leads to the possibility of predicting the type of solubility diagrams.

The dissertation is presented in eight sections, and in Section IX, X and XI the scientific contributions, publications on the topic and the doctoral student's participation in scientific forums are presented in turn. The volume of the dissertation is 139 standard pages, in which 199 references are cited, primarily in Latin. There are 30 tables and 24 figures. The structure of the dissertation fully complies with the requirements according to the RSPSSAD at "Prof. Dr. Asen Zlatarov" University of Burgas.

The literature review (Section II) presents known facts on the synthesis of selenate systems of mono- and divalent metals, characterization of the structure of selenates and double selenate salts, and investigation of their physicochemical properties. On this basis, the aim of the thesis – thermodynamic study of phase equilibria in metal selenate systems with a view to obtaining new salts – is clearly and precisely stated. The object of study are systems of alkali selenates and selenates of divalent metals, mainly of 3d-transition series. The formulated seven research tasks fully correspond to the set objective and concern: investigation of the solubility isotherms of selenate systems and determination of the composition of the obtained equilibrium phases, determination of the water activity at different concentrations of the components in the binary solutions of alkaline selenates by means of an isopiestic method and calculation of the osmotic coefficients and activity coefficients; determination of molar isobaric heat capacities and calculation of enthalpy and thermochemical potential of alkali selenates for different temperatures; Performing quantitative description of ternary systems, including both the ternary thermodynamic parameters (osmotic coefficients, activity coefficients, water activity, chemical potential, Gibbs energy, etc.) and theoretical calculation of solubility isotherms of ternary systems, combinations of the corresponding binaries.

In the third section of the thesis, "Development of thermodynamic studies of mixed solutions of strong electrolytes", the theoretical approach is presented and applied in order to derive quantitative regularities describing the complete state of the studied selenate systems with prediction possibilities and theoretical calculations of their solubility diagrams. The equilibrium patterns of mixed crystals and double salts from ternary aqueous-salt systems are described, as well as the methods for mutual calculation of activity coefficients and osmotic coefficients of electrolyte solutions (Gibbs-Duchem and Debye-Hückel equations). The thermodynamics of mixed solutions of strong electrolytes is characterized, the Pitzer method for binary and multicomponent systems and the approach for its application are presented, and information on the determination of some basic thermodynamic quantities – heat capacity, entropy, enthalpy, Gibbs energy is given.

The discussion of the results of the experimental and theoretical study of the synthesized selenate systems is presented in Section IV "Experimental data from equilibrium studies in ternary

water-salt selenate systems". The compositions of the existing equilibrium phases of the following 16 ternary selenate systems at 25°C have been studied: $Li_2SeO_4 - MgSeO_4 - H_2O$, $Li_2SeO_4 - CoSeO_4 - H_2O$, $Li_2SeO_4 - NiSeO_4 - H_2O$, $Na_2SeO_4 - MnSeO_4 - H_2O$, $Na_2SeO_4 - CoSeO_4 - H_2O$, $Na_2SeO_4 - NiSeO_4 - H_2O$, $Na_2SeO_4 - CuSeO_4 - H_2O$, $Na_2SeO_4 - ZnSeO_4 - H_2O$, $Na_2SeO_4 - CdSeO_4 - H_2O$, $Na_2SeO_4 - FeSeO_4 - H_2O$, $K_2SeO_4 - FeSeO_4 - H_2O$, $(NH_4)_2SeO_4 - FeSeO_4 - H_2O$, $Rb_2SeO_4 - ZnSeO_4 - H_2O$, $Cs_2SeO_4 - ZnSeO_4 - H_2O$, $Cs_2SeO_4 - NiSeO_4 - H_2O$, $Cs_2SeO_4 - CuSeO_4 - H_2O$. It was found that only pure salts from the systems crystallize at 25°C: $Li_2SeO_4 - MgSeO_4 - H_2O$, $Li_2SeO_4 - CoSeO_4 - H_2O$, $Li_2SeO_4 - NiSeO_4 - H_2O$ и $Na_2SeO_4 - NiSeO_4 - H_2O$. In the remaining selenate systems, double salts were obtained and the actual content of the components in the solid phase was determined by the Schreinemakers method and the crystallization water content by derivatographic analysis. X-ray phase analysis was also performed and interfacial distances were calculated. A comparison of the double salts obtained between analogous sulphates and selenates was made, from which it is evident that along with the ionic radii of the cations, the anions also play a role in the formation of the new structures.

In Section V of the dissertation, "Experimental Data from the Isopiastic Study of Selenate Systems", the activity-molality relationship of the component in binary solutions of alkali selenates is determined and the Pitzer method is applied to calculate activity coefficients in binary selenate systems. In connection with the latter, a computer program has been developed by means of which the activity coefficients of lithium, sodium, potassium, rubidium and cesium selenates in their binary unsaturated and saturated solutions have been calculated.

Data concerning the physicochemical characterization of the synthesized selenates are presented in Section VI "Heat capacities, enthalpy, entropy and thermochemical potential of selenate solid phases". Sample preparation for calorimetric studies, apparatus and the principle of the method are described. The molar isobaric heat capacities of five alkali selenates, eight divalent metal selenates and 34 double salts of selenates of the type $M_2SeO_4 \cdot MeSeO_4 \cdot xH_2O$ (where M = Li, Na, K, Rb, Cs, NH_4 and Me = Mg, Co, Ni, Fe, Cu, Zn, Mn, Cd). Based on the temperature dependence and standard entropy, the enthalpies and thermochemical potentials of the compounds were calculated for different temperatures.

Two methods are applied to estimate some thermodynamic parameters and interpret the solubility diagrams of selenate systems: 1) the Lietzke and Stoughton equations, a method further developed by Meissner and Kusick, and 2) the Pitzer method for quantitative description and theoretical calculation of solubility diagrams. As a result, the coefficients q (by the Meissner-Kussick equation), solubility product (lnПР) and Gibbs formation energy (G_f^o) were calculated for both the individual components and the double salts. The binary parameters in the Pitzer equations for five binary and for 25 ternary selenate systems were determined by regression analysis on data from isopiestic studies in the binary systems.

On the basis of the experimental and theoretical study of the 16 selenate systems, seven significant scientific contributions are outlined in Section IX of the thesis, corresponding to the results obtained. Some of the results relating to the study of phase equilibria in some of the selenate

systems were presented at two scientific forums in 1990, and others on the determination of thermodynamic properties and antitumor action of selenates were presented at two international conferences in 2021.

Three scientific publications have been submitted for this dissertation and are indexed in the world-renowned databases Scopus and Web of Science, respectively published in *Monatshefte für Chemie* in 1993 (1999: IF=0.377, Q2, 20 pts.), *Chemical Data Collections* in 2021 (IF=0.2017, Q3, 15 pts.) and *Journal of Molecular Structure* (2021: IF=0.48, Q2, 20 pts.). All three publications are co-authored with the academic advisor and reflect the thesis topics of the PhD programme in Inorganic Chemistry.

In accordance with the minimum national requirements and The Regulation of the Terms and Procedure for Acquisition of Academic Degrees at "Prof. D-r Asen Zlatarov" University of Burgas, the required minimum for the award of PhD in the professional field of Chemical Sciences is 80 points – 50 points for the presentation of a dissertation (group of indicators A) and 30 points (group of indicators Г). The scientific production of Dencho Mihov under item 7 of "group of indicators Г" (scientific publications in publications that are refereed and indexed in world-known databases with scientific information Scopus and Web of Science) amounts to 55 points, which brings the total of 105 points as a fulfilled requirement for the award of the PhD in the professional field 4.2. Chemical sciences.

3. Conclusion

The dissertation discusses a topical scientific problem focused on theoretical and experimental studies of selenate systems of monovalent and divalent metals. The results of these studies contribute to the development of science in applied aspect in various fields - electrochemistry, medicine, agriculture, semiconductor engineering, etc. I believe that the research work is well planned and successfully implemented by the PhD student. My personal impression, gained as a result of his two years of training and conducting research work in the Department of Chemistry, is that Eng. Dencho Mihov possesses in-depth theoretical knowledge and professional skills enabling him to independently conduct scientific research in the field of inorganic chemistry.

In view of the above, I confidently give my positive assessment of the research, the results and the outlined contributions of the thesis. I vote "YES" for the award of the PhD degree in Inorganic Chemistry to Eng. Dencho Ivanov Mihov in the ares of higher education 4. Natural Sciences, Mathematics and Informatics, professional field 4.2 Chemical Sciences.

Подпис заличен
Чл.2 от ЗЗЛД

16.12.2022 Scientific Jury Member:

Assoc. Prof. Svetlana Zheleva, PhD