REVIEW

by

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Regarding

the defense of dissertation for academic and scientific PhD degree, Area of Higher Education 4. Natural Sciences, Mathematics and Informatics, Professional Field 4.2 Chemical Sciences, Doctoral Program 01.05.02. Inorganic Chemistry, for the needs of the Faculty of Natural Sciences, "Asen Zlatarov" University of Burgas.

By order № УД-289/ 26.10.2022 signed by the Rector of Asen Zlatarov University of Burgas I'm appointed as a member of the scientific jury. At its first meeting on 07.11.2022 I was chosen to write a review, which is in accordance with The Regulation on the Terms and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Jobs at University of Burgas.

Eng. Dencho Ivanov Mihov is the sole applicant for the PhD degree at Department of Chemistry, Faculty of Natural Sciences, "Asen Zlatarov" University of Burgas. I have received electronically and hard copy of all materials for the competition.

Brief Biographical Data

In 1988 Eng. Dencho Ivanov Mihov was awarded a Master Degree in Chemical Engineering at Asen Zlatarov University of Burgas. In the period from 1988 to 1999 he is an assistant, and chef assistant at Prof. Assen Zlatarov University of Burgas. From 2002 till now he is a chief of "Libra Scorp" publishing house. Since 2021 Dencho Mihov is a PhD student at Department of Chemistry, Faculty of Natural Sciences, "Asen Zlatarov" University of Burgas, Doctoral Program 01.05.02. Inorganic Chemistry.

Scientific contributions

The title of presented dissertation is " Experimental and theoretical studies of selenate systems". The Academic Advisor of dissertation is Assoc. Prof. Eng. Rumyana Yankova-

Avramova, PhD. Dr. Yankova is an expert with a long time experience and impressive list of publications in studies of selenite solutions and solid phases. The dissertation contains 143 typewritten pages, including 30 tables, 24 figures, a list of 199 references, 169 in Latin and 30 in Cyrillic.

For the needs of the chemical industry and modern technology, inorganic salts of technical, chemical and special purity are required. The production of salts is most often based on multicomponent systems. In this case, the first and fundamental problem to be solved is to determine the equilibrium existence field of the given salt in the multicomponent system. The second problem is the question of the purity of the resulting salts, i.e. which of the impurities present in the solution, and to what extent, are incorporated into the final product. To solve these industrial problems, it is necessary to complete experimental solubility database for mixed systems and to develop theoretical thermodynamic solid-liquid equilibrium models, which are based on experimental results obtained. The presented dissertation contributes significantly in chemical production industry of pure selenate solid phases (simple and double salts, solid solutions).

The aim of the dissertation can be summarized as fellow: 1) thermodynamic study of phase equilibria in metal selenate systems with a view to obtaining new salts. The object of study are systems of the type: $M_2SeO_4 - MeSeO_4 - H_2O$ (where M = Li, Na, K, Rb, Cs, NH_4, and Me = Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd), i.e., a combination of alkali selenates and selenates of divalent metals, mainly of the first order of transition metals. 2) to obtain new experimental data describing aqueous solutions of selenates; 3) to derive quantitative laws describing the complete state of these systems with predictive capabilities and theoretical calculations of their solubility diagrams. 4) From the experimental data on the activity coefficients of the binary solutions, to make a quantitative description of the ternary systems, including both the ternary thermodynamic parameters (osmotic coefficients, activity coefficients, water activity, chemical potential, Gibbs energy, etc.) and a theoretical calculation of the solubility isotherms of the ternary systems, combinations of the respective binary.

The conclusions of dissertation are correctly formulated as:

1. Under isothermal conditions (T = 25°C) were studied the solubility isotherms of 16 systems of the type $Me_2SeO_4 - Me'SeO_4 - H_2O$ ($Li_2SeO_4 - MgSeO_4 - H_2O$, $Li_2SeO_4 - CoSeO_4 - H_2O$, $Li_2SeO_4 - NiSeO_4 - H_2O$, $Na_2SeO_4 - MnSeO_4 - H_2O$, $Na_2SeO_4 - CoSeO_4 -$

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 and the compositions of the crystallising equilibrium phases have been determined over the whole concentration range of the components.

2. It has been shown that lithium selenate systems and systems Na_2SeO_4 – $MnSeO_4$ – H_2O and Na_2SeO_4 – $NiSeO_4$ – H_2O are of the simple eutonic type, and in the rest double salts are formed and the region of their equilibrium existence is determined.

3. The composition of the double salts was determined by physicochemical analysis using the Schreinemakers method and by derivatographic analysis. X-ray powder analysis of the double salts was also performed.

4. The activity of water at different concentrations of the components in the binary solutions of five alkali selenates was determined by the isopiestic method (Li_2SeO_4 – H_2O, Na_2SeO_4 – H_2O, K_2SeO_4 – H_2O, $(NH_4)_2SeO_4$ – H_2O, Rb_2SeO_4 – H_2O, Cs_2SeO_4 – H_2O), the osmotic and activity coefficients have been calculated.

5. The molar isobaric heat capacities of five alkali selenates have been determined by differential scanning calorimetry (Cp, J/mol.K). The least squares method is used to determine the empirical coefficients in the equation $Cp = a + bT + cT^{-2}$. Based on the temperature dependence and standard entropy, the enthalpies and thermochemical potentials of the compounds were calculated for different temperatures.

6. Cusick and Meissner's equations are fitted to interpret the triple systems. The coefficients q are calculated (by the Meissner-Cussick equation). Solubility products (lnPr), and Gibbs energy of formation (G^o_f) were calculated for the individual components and for the double salts

7. The binary parameters in the Pitzer equations have been determined for five binary and 25 ternary selenate systems by regression analysis on isopiestic data in the binary systems

The abstract has a total of 76 pages and complies with the requirements of the Law. The abstract correctly describes the main goals and contributions of the thesis. Some part of results is also reported in 4 scientific forums in Bulgaria.

Meeting the Minimum National Requirement

The set of materials submitted by Mr. Mihov is in compliance with The Regulation on the Terms and Procedure for Acquisition of Academic Degrees at "Asen Zlatarov" University of Burgas and includes all administrative and scientific documents required.

Eng. Dencho Mihov submits for the completion a total list of 3 publications (Web of Science и Scopus, SJR).

It should be noted that all 3 publications are co-authored with scientific advisor- R. Yankova.

1. Ojkova T., D. Michov, R. Jankova. Dreistoffsysteme Wasser-Salz mit Lithiumselenat, Natriumselenat, Kobaltselenat und Magnesiumselenat bei 25°C (The triple system water-salt with lithium selenate, sodium selenate, cobalt selenate or magnesium selenate at 25°C). Monatshefte für Chemie – Chemical Monthly, 1993, ISSN 0026-9247, 124, pp. 349–354 (1999: Q2 – 20 т.).

2. Mihov, D., R. Yankova. Crystal structure, IR investigation and interpretation of interactions in cobalt selenate pentahydrate. Chemical Data Collections, 2021, ISSN 2405-8300, 36, pp. 100776. (2021: Q3 – 15 т.).

3. Yankova R., I. Tankov, D. Mihov, A. Kostadinova. Coordination metal effect on the nonlinear optical properties and biological activity of double selenates. Journal of Molecular Structure, 2022, ISSN 0022-2860, 1268, pp. 133712. (2021: Q2 – 20 т.).

According to the regulations procedures in professional field 4.2 Chemical sciences involve quartiles Q1, Q2, Q3 and Q4 according to the metrics SJR. In this regard Dencho Mihov submitted 2 publications Q2 (40 points); and 1 publ. Q3 (15 p.) – (total **55 p).**

According to the analysis of the results the minimum number of points (30 points) required for the PhD degree in the professional field 4.2 Chemical Sciences, according to the Minimal National Requirements, and Regulations for the development of the academic staff of Asen Zlatarov" University of Burgas are met.

Considering the volume of presented in dissertation experimental material and theoretical models, I suggest that the applicant is an author of other publications, not included in the publication list to the dissertation. Analyzing the theoretical and practical importance of the research area, and the promising results obtained within the doctoral study, I can recommend to continue and to deep the research of presented dissertation.

CONSLUSION

Once I have read the materials and scientific publications submitted and have made an analysis of their significance and the scientific contributions contained in them, I think that the candidate Eng. Dencho Mihov has accomplished the minimal national requirements set in the Republic of Bulgaria, The Regulation on the Terms and Procedure for Acquisition of Academic Degrees and the Occupation of Academic Jobs at "Asen Zlatarov" University of Burgas, and all other relative normative documents. I find it worthwhile **to give my positive assessment** and to recommend to the Scientific Jury to grant the educational and scientific PhD degree to Eng. Dencho Mihov at "Asen Zlatarov" University of Burgas in the Area of Higher Education 4. Natural Sciences, Mathematics and Informatics, Professional Field 4.2 Chemical Sciences (Inorganic Chemistry). I believe that Dencho Mihov will have a successful and productive scientific work in the future.

Подпис заличен
Чл.2 от ЗЗЛД

08.12. 2022

Scientific Jury Member:

(Prof. Christomir Christov, DSci)