ROMANIAN ACADEMY

„Ilie Murgulescu" Institute of Physical Chemistry

DOCTORAL THESIS

ABSTRACT

TERMODYNAMICS CHARACTERIZATION OF SOME AMINO ACIDS AND THEIR DERIVATIVES

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CONTENT

KEYWORDS: Amino Acid, Cation, DSC, Combustion Calorimetry.

INTRODUCTION

Amino acids are the fundamental constituents of living matter. They are involved in numerous biochemical processes such as metabolism, enzymatic catalysis, hormone synthesis, etc. The study of amino acids and their derivatives represent a vast area of research. Structure and control of their properties find important applications in medicine, the pharmaceutical industry or the food industry and provides structural chemistry, thermodynamics and kinetics of a precious study material. Thus, amino acids and their derivatives represent an interface of immediate and future importance between biology, materials science and nanotechnology.

As part of these surveys, the determination of the thermodynamic data relating to the conditions of stability, as well as the study of the correlation between the thermodynamic properties and various compositional variables are needed. A systematic thermodynamic study based on quantitative experimental data is very important so much the more for some systems there are discrepancies between characteristic thermodynamic functions, while for a number of derivatives, there are no experimental data on the combustion and formation enthalpies that are essential for establishing the domains of stability.

To bring original contributions to the proposed theme, in this thesis a systematic study of the thermodynamic stability domains and of the correlations existing between composition, structure and thermodynamic behavior of amino acids and their derivatives in solid form was performed.

For this study were selected the following amino acids: glycine, L-alanine, L-serine, L-threonine, L-proline and L-glutamine. Starting from these amino acids, their corresponding nitrates have been synthesized; from serine and alanine have been also synthesized their ethyl esters nitrates.

In order to achieve the PhD Thesis aim, the following objectives have been fulfilled:

1. *The study of the thermochemical properties of the amino acids: glycine, L-alanine, L-serine, L-threonine, L-proline and L-glutamine* by *combustion calorimetry and differential scanning calorimetry in both isothermal and dynamic modes.* **The thermochemical behavior has been investigated in the temperature range of 300 – 523 K. The temperature of phase transformations has been determined and the values of the thermodynamic properties represented by the enthalpies of combustion, standard enthalpies of formation, heat capacities and enthalpies of melting and/or decomposition of the studied aminoacids have been evaluated. The thermodynamic stability domains and the correlation structure - thermodynamic properties have been evidenced.**
2. *Synthesis of the following derivatives: - glycine, L-alanine, L-serine, L-threonine, L-proline and L-glutamine nitrates; - alanine and serine ethyl ester nitrates.* During this study **the glutamine nitrate and L-serine ethyl ester nitrate has been synthesized for the first time**.

3. *Polarimetry determinations* ***for checking the chirality of the asymmetric atom of carbon for the synthesized nitrates.***
4. *The study of the thermochemical properties of the derivatives synthesized in the laboratory.* The enthalpies of combustion and the standard enthalpies of formation for all the derivatives and the heat capacity of glycine and alanine nitrates have been determined for the first time in the frame of this Thesis. ***The study allows for the determination of the stability domains and gives information on the temperatures and enthalpies of melting and decomposition.***
5. Complementary experimental investigations to obtain further information on the composition-structure-properties correlation through the use of appropriate experimental techniques namely, x-ray diffractograms, Raman and FTIR Spectroscopy, UV–Vis Spectrophotometry.
6. Highlighting the influence of the amino acid or ester of amino acids cations on the thermochemical properties of derivatives by comparison with the properties of amino acids used in synthesis.
7. The identification of possible applications of the synthesized semi-organic compounds based on the experimentally investigated properties.

Structure of the thesis:

The doctoral thesis is structured into eight chapters included in three distinct parts:

Part I: The state of the art of research in the PhD Thesis field. (chapters 1 and 2)

Part II: Experimental methods and techniques of characterization (Chapter 3)

Part III: Original Contributions (chapters 4, 5, 6, 7, 8)

The thesis concludes with a chapter of Concluding remarks (chapter 8), followed by the bibliographic references and appendices.

Chapter 1, Introduction, contains information relating to the characteristic and importance of amino acids and their derivaties. In the introduction are also presented the purpose, specific objectives and the structure of the thesis.

Chapter 2 contains a description of the current status of research on amino acids and their derivatives, with special emphasis placed on the main theoretical and experimental aspects related to amino acids thermochemical study. It identifies the need for contributions in this area.

Chapter 3 contains the presentation of the experimental physico-chemical characterization methods and techniques, insisting on the methods used thermodynamic characterization.

Chapter 4 contains the presentation of the methods of synthesis of the studied compounds.

Chapter 5 contains the results of structural characterization measurements (X-rays diffraction, Raman and IR Spectroscopy, UV–Vis Spectrophotometry, Polarimetry).

Chapter 6 contains original contributions and experimental results obtained from the thermochemical study conducted on the amino acids (glycine, L-alanine, L-serine, L-threonine, L-proline and L-glutamine) and the derivatives (nitrate of glycine, L-alanine nitrogen, nitrate nitrogen, L-threonine L-proline and L-glutamine nitrate and ethyl ester nitrates of L-alanines and L-serines). Thermochemical characterization was done by Combustion Calorimetry and Differential Scanning Calorimetry in both dynamic and isothermal modes (by power compensation DSC and C80 Calvet Calorimeter). Results concerning the thermodynamic stability (the enthalpies of combustion and the formation in standard state, heat capacity, the enthalpies of melting and/or decomposition) are presented.

Chapter 7 contains a comparative discussion of the thermodynamic stability of the studied amino acids and derivatives. It was analyzed the influence of the various structural variables (nitrate anion, amino acid cation) on the thermochemical properties of nitrogen derivatives and the correlation between these properties and the chemical structure.

Chapter 8 containes the general conclusions resulted from the present study.

The thesis ends with bibliographic references and appendices containing information on positions and assigns of FTIR and the Raman spectra of the studied compounds.

Results of the structural and thermochemical characterization of the studied materials are presented below.

STRUCTURAL CHARACTERIZATION OF AMINO ACIDS AND DERIVATIVES

Before the thermochemical study, the structural characterization of the amino acids and synthesized derivatives has been performed. To this end, we used the following experimental methods:

- Polarimetry for keep checking chirality of the asymmetrical carbon atom in the nitrates synthesized in the laboratory.
- X-ray diffraction of crystalline compounds (Gly, Ala and their derivatives $GlyNO_3$, $AlaNO_3$) for determining the structure of crystalline lattices;
- IR and Raman spectroscopy, attributing the main peaks and their positions in their respective spectra;
- UV–Vis spectroscopy for optical transparency highlighting of the synthesized compounds;

The results of the derivatives study will be considered by correlation with the results obtained in the study of pure amino acids.

The vast majority of amino acids with formula NH_2–CHR–COOH (where R may be CH_3, OH, etc.) have asymmetric α-carbon atom. The exception to this rule is even the smallest amino acid, namely glycine. It was found that such a large proportion of the amino acids in the free state (except proline, arginine) exist in the form of dipolar: NH_3^+–CHR–COO^-.

Given the dependence of property and structural stability in condensed state of amino acids and of their derivatives on the van der Waals interactions and hydrogen bonds in their dipole molecules (groupings COO^- and NH_3^+), IR and Raman spectroscopy are two important vibrational techniques to investigate structural dynamics, especially hydrogen bonds.

Almost all amino acids excepting glycine (Gly), contain chirals carbon atoms and crystallizes in the space group with no central symmetry, being optical active. Due to the nature of the dipole, NH_3^+ and COO^-, amino acids have been considered ideal candidates for nonlinear optical uses, so-called NLO applications. In addition to the structural identification of amino-acids and their salts, vibrational-spectroscopy (IR and Raman) is also used to determine the correlation structure– hiperpolarizability–nonlinear response.

UV-Vis Spectrophotometry measurements for amino acid derivatives

According to the UV-visible spectra, all studied compounds of the $AANO_3$ type have a wide range of transparency (Fig.1) and a low value of "cut off".

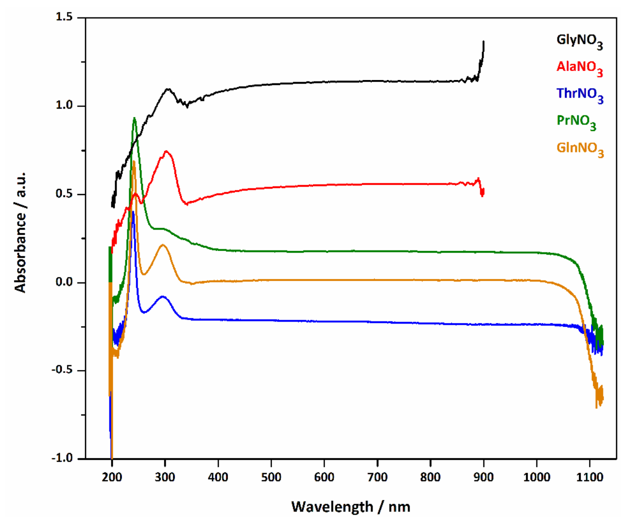

Fig. 1 UV-Vis spectra for nitrates type $AANO_3$

The absence of transparency in the visible region (small value of "cut-off") is an intrinsic property of amino-acids which can be used in applications NLO.
Consistent with the results obtained from the DSC as concerns the melting temperatures or decomposition of compounds, one can specify temperature field in that nitrates of amino acids can be used in applications such as lasers.

THERMOCHEMICAL STUDY OF AMINO ACIDS

To perform a systematic study, in the first phase have been investigated amino acids that have been used in the synthesis of nitrogen derivatives namely: glycine and alanine (aliphatic amino acids differing between them through a methyl group $-CH_3$); serine and threonine (hydroxy amino acids), proline (a cycle of five atoms, one being the nitrogen atom, so it is a secondary amine in the AA molecule); glutamine (amide group in a position of γ). It is stated that all amino acids used were stereoisomers type L (Left-handed). In the next stage, their derivatives namely nitrates $AANO_3$ and ethyl esters nitrates AAC_2NO_3 were studied.

The thermochemical study of amino acids aims:

- Determination of thermochemical properties represented by enthalpy of combustion and the formation in standard state.
- Determination of heat capacity for glycine and L-alanine in the temperature domain of 310.15 – 373.15K.
- Defining the domain of the stability and the thermal behavior in temperature range 300 – 623 K for glycine and alanine; 300 – 600 K for proline, respectively 300 – 523 K for serine, threonine, glutamine.
- Obtaining the enthalpies of melting or decomposition corresponding thermal effects that occur as a result of the heat treatment of the studied amino acids.

The values obtained for thermochemical properties [***A. Neacşu, D. Gheorghe, I. Contineanu, S. Tănăsescu Şt. Perişanu, A thermochemical study of serine stereisomers, Thermochim. Acta (2014) 595, 1-5; I. Contineanu, A. Neacşu, D. Gheorghe, S.Tănăsescu, Şt. Perişanu, The thermochemistry of threonine stereisomers, Thermochim. Acta (2013) 563, 1–5***] were compared with the literature data. The need for reevaluation of the amino acids and their study was required by the existence of inconsistencies in the literature values for the same compound.

THERMOCHEMICAL STUDY OF THE AMINO ACIDS DERIVATIVES

In this thesis were determined for the first time enthalpies of combustion and formation of the compounds synthesized: $GlyNO_3$, $AlaNO_3$, $ThrNO_3$, $ProNO_3$, $GlnNO_3$, $AlaC_2NO_3$, $SerC_2NO_3$. It has to be mentioned that $GlnNO_3$ and $SerC_2NO_3$ were prepared for the first time.

For the thermochemical study, the following experimental techniques were used:

- Combustion Calorimetry – to determine the enthalpies of combustion and the enthalpy of formation of the derivatives.
- Thermal analysis (DSC) for determining transformations and transitions at temperature increasing; the possible thermal effects (melting, decomposition) have been identified, and their characteristics (temperatures and enthalpies) were determined. The temperature was monitored to define the domain in which the synthesized compounds were thermally stable and can be used in various applications, such as lasers or various optoelectronic devices.
- Determination of molar heat capacity for $GlyNO_3$ and $AlaNO_3$ was performed using C80 calorimeter.
- The working conditions for all thermal analysis experiments were the same as for amino acids.
- The investigated temperature domain was 200 – 523 K for all synthesized derivatives of the amino acids.
- The results of the derivatives study have been correlated with those obtained in the study of pure aminoacids. [***D. Gheorghe, A. Neacşu, I. Contineanu, F. Teodorescu, S. Tănăsescu, Thermochemical properties of L-alanine nitrate and L-alanine ethyl ester nitrate, J. Therm. Anal. Calorim. (2014) 118 (2), 731-737***]

DISCUSSION ON THERMAL STABILITY AND THERMODYNAMICS OF THE STUDIED COMPOUNDS

Correlations between chemical structure and thermochemical properties

The knowledge of the stability domains of amino acids and their derivatives is important both from the point of view of fundamental research, but above all it is necessary for defining the areas of temperature in which compounds can be used in different applications.

Characteristic for the thermal behavior of the amino acids is that they are thermodynamic stable until appearance of the first heating effect attributed to the melting. This effect is followed by a endothermic process attributed to decomposition with a consistent loss of mass. Position and nature of the side chain lead to changes of thermal stability, as well as of the process of decomposition.

- ❖ Considering the enthalpy of formation, $\Delta_f H^o$ as the defining thermodynamic stability of compounds, in the diagram in Fig.2 a comparison of the degree of stability of the different amino acids is presented. Stability varies as follows: Gly<Pr<Ala<Ser<Thr<Gln.

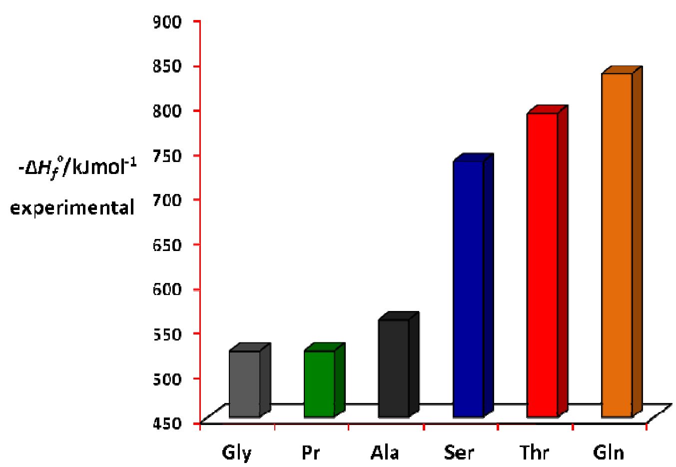

Fig. 2 Stability of the studied amino acids— **Gly<Pr<Ala<Ser<Thr<Gln**

Glycine stability has the smallest in the amino acid study series. Proline is a secondary amine with a cycle of five atoms, one nitrogen Atom being and there are no extra hydrogen bonds out of this cycle. Although the standard formation enthalpies, $\Delta_f H^o$ of glycine and alanine have values near each other, alanine stability is still higher as compared to glycine, it containing a group $-CH_3$ in addition.

Serine has the value of standard enthalpy of formation smaller in absolute value than the threonine, the latter containing a group $-CH_3$ in addition to serine. Thermal stability of threonine compared with serine is also confirmed by the higher values of temperature and enthalpy of decomposition. [***A. Neacşu, D. Gheorghe, I. Contineanu, S. Tănăsescu Şt. Perişanu, A thermochemical study of serine stereisomers, Thermochim. Acta (2014) 595, 1-5; I. Contineanu, A. Neacşu, D. Gheorghe, S.Tănăsescu, Şt. Perişanu, The thermochemistry of threonine stereisomers, Thermochim. Acta (2013) 563, 1–5***].

In the series of the studied amino acids, glutamine showing a group amide in γ position has the standard enthalpy of formation with the highest absolute value indicating the highest stability. This is explained by the existence of five hydrogen bonds per molecule, one for each H atom — two from the amide NH_2 group and three from the NH_3^+ group in zwiterion, adding to it and the bond type N^+—H...$^-$O=C, one of the most powerful existing intermolecular interactions of biological compounds.

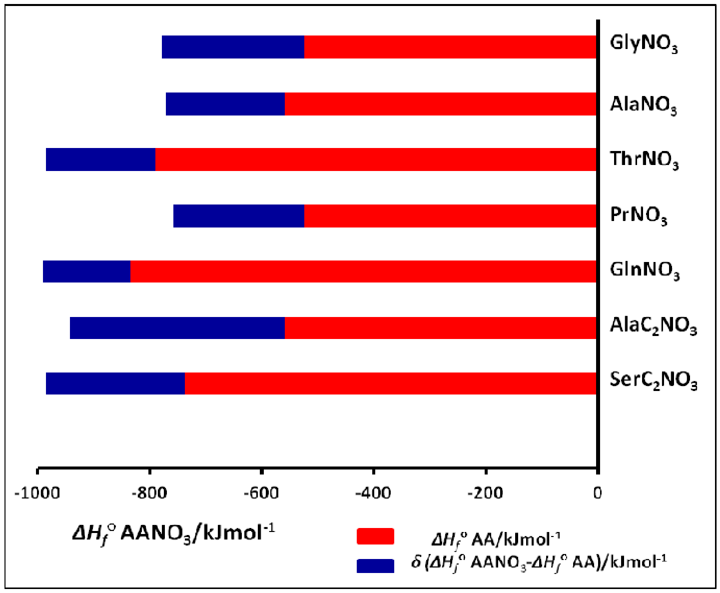

Fig.3 Stability of amino acid nitrates derivatives
$PrNO_3$<$AlaNO_3$<$GlyNO_3$<$AlaC_2NO_3$<$ThrNO_3$<$GlnNO_3$<$SerC_2NO_3$

- Derivatives have a greater stability than the amino acid from which they originate, in order varying stability of $PrNO_3$<$AlaNO_3$<$GlyNO_3$<$ThrNO_3$<$GlnNO_3$. In the study, the ethyl esters derivatives have the highest stability (Fig.3). Higher stability is demonstrated by the amount of enthalpy of formation which can be put on the cation-anion interaction being stronger. Contribution of enthalpy of formation of the enthalpy of the amino compound derived predominates in all cases (Fig.3). [***D. Gheorghe**, A. Neacşu, D. Drăgoescu, I. Contineanu, S. Tănăsescu, Thermochemical and Thermophysical Properties of some Nitrates with Amino Acids Cation, International Conference of Physical Chemistry (ROMPHYSCHEM 15), 11-13 Septembrie 2013, Bucureşti, România*]
- The nitrates have high energies of decomposition (Fig. 4) due to the thermal instability induced by NO_3^- ion. It should be noted that the exothermic decomposition is influenced by the presence of an additional functional group that determines the decreasing of the decomposition temperatures and changes in the developed energy.

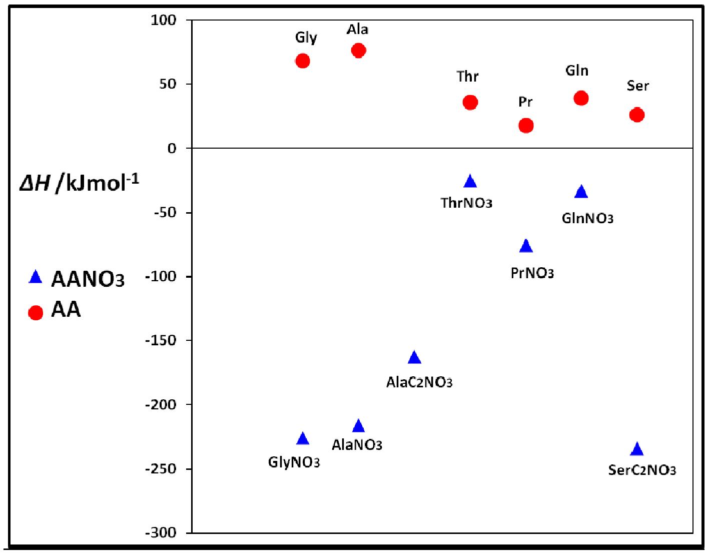

Fig. 4 Enthalpy of decomposition, *ΔH*, amino acids (AA) and derivatives ($AANO_3$)

- In the case of compounds containing cation alanine it was noted that stability increases as the anion-cation interactions become stronger than the hydrogen bonds, so that stability varies according to Ala<$AlaNO_3$<$AlaC_2NO_3$. [***D. Gheorghe**, A. Neacşu, I. Contineanu, F. Teodorescu, S. Tănăsescu, Thermochemical properties of L-alanine nitrate and L-alanine ethyl ester nitrate, J. Therm. Anal. Calorim. (2014) 118 (2), 731-737*].
- Presence group –OH bound to a primary carbon, as in the case of the serine molecule, has a stabilizing effect which manifests also in the case of the ethyl ester of serine nitrate, its formation enthalpy being higher than $AlaC_2NO_3$.
- Almost all amino acids except glycine (Gly), contain chiral carbon atoms and crystallizes in the space group withought central symmetry, being optical active. Due to the dipolar nature, NH_3^+ and COO^-, amino acids have been considered ideal candidates for nonlinear optical applications. Study in the thesis outlined the domains of stability of the new compounds synthesized in the laboratory, ideal candidates for optical applications.

GENERAL CONCLUSIONS

The study led to the following conclusions and original contributions:

- Taking into account the existing discrepancies in the literature between the values of the enthalpies of formation and combustion for simple amino acids, their thermochemical data have been updated and the correlation between structure and thermodynamic properties of amino acids have been evidenced.
- Enthalpies of combustion and formation of nitrates were determined for the first time in the framework of this thesis, the obtained results completing thermochemical databases for derivatives of amino acids.
- The enthalpies values of the studied compounds demonstrate their high stability.

- The influence of the chemical structure of the amino acid cation on the thermochemical properties of the synthesized derivatives has been evidenced.
- The feasibility of synthesis and stability of the compounds synthesized have been proved by the obtained values of the enthalpies of formation. The same is true for the ethyl esters of nitrates. Investigation of the behavior to heating by differential scanning Calorimetry provided information on: solid-liquid transition temperatures and enthalpies (melting) and solid-gas (decomposition).
- An exothermic decomposition is characteristic for nitrates due to release of large quantities of gas from decomposition, confirmed by the considerable loss of mass. Comparison of characteristic peak temperatures recorded in termograms of amino acids with those of the corresponding nitrates show, without exception, a shift with more than 100 ^{0} to lower values for nitrates. Lower temperatures and the associated effects of the enthalpies changes is made on account of the change of the number of hydrogen bonds between the molecules of the derivative.
- It should be mentioned that the ethyl esters of serine and alanine nitrates have melting point below 100 ^{0}C and can be considered as ionic liquids.

Experimental complementary methods were used to obtain further information on the crystalline structure, optical properties, optical activity, through the use of appropriate experimental techniques namely, XRD, IR and Raman Spectroscopy, UV-Vis spectrophotometry, Polarimetry.

List of scientific papers published in specialized journals listed in ISI system, about the theme of the thesis

1. D. Gheorghe, A. Neacşu, I. Contineanu, F. Teodorescu, S. Tănăsescu, Thermochemical properties of L-alanine nitrate and L-alanine ethyl ester nitrate, J. Therm. Anal. Calorim. (2014) 118 (2), 731-737. (F.I. 2013-2.206)
2. A. Neacşu, D. Gheorghe, I. Contineanu, S. Tănăsescu Şt. Perişanu, A thermochemical study of serine stereisomers, Thermochim. Acta (2014) 595, 1-5. (F.I. 2013-2.105)
3. I. Contineanu, A. Neacşu, D. Gheorghe, S.Tănăsescu, Şt. Perişanu, The thermochemistry of threonine stereisomers, Thermochim. Acta (2013) 563, 1–5. (F.I. 2013-2.105)

Other papers published in specialized journals listed in ISI system

1. D. Dragoescu, D. Gheorghe, M. Bendová, Z. Wagner, Speeds of sound, isentropic compressibilities and refractive indices for some binary mixtures of nitromethane with chloroalkane at temperatures from 298.15 to 318.15 K. Comparison with theories, Fluid Phase Equilib. (2015) 385, 105-119**.** (F.I. 2013-2.241)
2. D. Gheorghe, D. Dragoescu, M. Teodorescu, Volumetric Study for the Binary Nitromethane with Chloroalkane Mixtures at Temperatures in the Range (298.15 to 318.15) K, J. Chem. Eng. Data (2013) 58 (5), 1161–1167. (F.I. 2.045)
3. D. Dragoescu, M. Teodorescu, D. Gheorghe, Isothermal vapor-liquid equilibria and excess Gibbs free energies in some binary nitroalkane+chloroalkane mixtures

at temperatures from 298.15K to 318.15K, Fluid Phase Equilib. (2013) 338, 16-22. (F.I. 2.379)

4. M. Teodorescu, D. Dragoescu, D. Gheorghe, Isothermal (vapour + liquid) equilibria for (nitromethane or nitroethane + 1,4-dichlorobutane) binary systems at temperatures between (343.15 and 363.15) K, J. Chem. Thermodyn. (2013) 56, 32-37. (F.I. 2.297)
5. M. Teodorescu, A. Barhala, D. Dragoescu, D. Gheorghe, Isothermal Vapor–Liquid Equilibria for Nitromethane and Nitroethane + 1,3-Dichloropropane Binary Systems at Temperatures between (343.15 and 363.15) K, J. Chem. Eng. Data, (2011) 56 (12) 4665–4671. (F.I. 1.693)
6. D. Dragoescu, A. Barhala, M. Teodorescu, D. Chiscan, Isothermal vapour-liquid equilibria in cyclohexanone + dichloroalkane binary mixtures at temperatures from 298.15 to 318.15 K, J. Serb. Chem. Soc. (2011) 76 (2) 305-315. (F.I. 0.879)

List of papers presented at international scientific events

1. D. Gheorghe, A. Neacşu, I. Contineanu, F. Teodorescu, S. Tănăsescu, Thermochemical properties of L-alanine nitrate and L-alanine ethyl ester nitrate, Eastern European Conference on Thermal Analysis and Calorimetry (CEEC-TAC2), August 26 – 30, 2013, Vilnius, Lituania. (poster)
2. D. Gheorghe, A. Neacşu, D. Drăgoescu, I. Contineanu, S. Tănăsescu, Thermochemical and Thermophysical Properties of some Nitrates with Amino Acids Cation, International Conference of Physical Chemistry (ROMPHYSCHEM 15), September 11-13, 2013, Bucharest, Romania. (poster)
3. A. Neacşu, D. Gheorghe, I. Contineanu, Şt. Perişanu, M. Contineanu, S. Tănăsescu, The calorimetric study of stereoisomers of irradiated and non irradiated serine, International Conference of Physical Chemistry (ROMPHYSCHEM 15), September 11-13, 2013, Bucharest, Romania. (oral communication)
4. D. Gheorghe, D. Drăgoescu, A. Neacşu, S. Tănăsescu, Enthalpies of dissolution for two amino acid nitrates in water, International Conference of Physical Chemistry (ROMPHYSCHEM 15), September 11-13, 2013, Bucharest, Romania. (poster)
5. D. Drăgoescu, D. Gheorghe, Densities and excess molar volumes for the binary mixtures of nitroethane with chloroalkane at temperatures between (298.15 and 318.15) K, International Conference of Physical Chemistry (ROMPHYSCHEM 15), September 11-13, 2013, Bucharest, Romania. (poster)
6. D. Drăgoescu, D. Gheorghe, Speed of sound, isentropic compressibility and refractive index for nitromethane with chloroalkane binary mixtures at temperatures of 298.15- 318.15 K, International Conference of Physical Chemistry (ROMPHYSCHEM 15), September 11-13, 2013, Bucharest, Romania. (poster)
7. C. Marinescu F. Teodorescu, D. Chiscan, S. Tănăsescu, Investigation of the correlation between the nonstoichiometry and the thermodynamic properties of some SOFC materials, "International Summer School on Fuel Cells – Fundamentals –Materials & Electrochemical Aspects", July 17-20, 2007, Sibiu, România. (poster)

List of papers presented at national scientific events

1. D. Gheorghe, A. Neacşu, I. Contineanu, Şt. Perişanu, S. Tănăsescu, The calorimetric study of L-, and D- isomers of tryptophan, The 23rd Symposium of Thermal Analysis and Calorimetry, February 14th, 2014, Romanian Academy, Bucharest. (oral communication)
2. D. Gheorghe, A. Neacşu, I. Contineanu, S. Tănăsescu, Şt. Perişanu, The calorimetric study of L-, D- and DL- isomers of serine, The 22th Symposium of Thermal Analysis and Calorimetry, February 15th, 2013, Romanian Academy, Bucharest. (oral communication)
3. D. Gheorghe, A. Neacşu, I. Contineanu, S. Tănăsescu, The calorimetric study of some nitrates with amino acids cation, Simpozion ICECHIM "Priorităţile chimiei pentru o dezvoltare durabilă"- PRIORCHEM - ed. a VIII-a, October 25-26, 2012, Bucharest. (poster)
4. D. Gheorghe, D. Drăgoescu, M. Teodorescu, A. Neacşu, S. Tănăsescu, Heat of dissolution for two green ionic liquids in water, Thermal Analysis and Calorimetry Techniques Workshop, "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, September 26-27, 2012, Bucharest. (poster)

Training courses

1. "International Seminar HEAT CAPACITY: METHODS AND MEASUREMENTS", October 1st, 2013, Prague, Czech Republic.
2. "Latest measurement applications thermal analysis, gas sorption, calorimetry and thermal conductivity- companies SETARAM and C-Therm", October 2nd, 2013, Prague, Czech Republic.
3. "Short Summer School on Thermal Analysis and Calorimetry", August 26th, 2013, Vilnius, Lituania.
4. "Thermal Analysis and Calorimetry Techniques Workshop", "Ilie Murgulescu" Institute of Physical Chemistry, Romanian Academy, 26-27 September 2012, Bucharest, organized by companies SETARAM.
5. "Techniques for the characterization of pharmaceuticals and biological samples", May 24th, 2011, "Ilie Murgulescu" Institute of Physical Chemistry, organized by Amex Import Export SRL.
6. "International Summer School on Fuel Cells – Fundamentals –Materials & Electrochemical Aspects", July 17-20, 2007, Sibiu, Romania, organized by "Ovidius" University from Constanta.