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QUANTUM-CHEMICAL MODELING OF URONATE POLYSACCHARIDES DIMERS IN THE STRATEGY OF CREATING FOOD BIODEGRADATED COATINGS

В статті розглянуті важливі аспекти комп'ютерного моделювання процесів, що протікають при утворенні гелів харчових плівкоутворюючих. Наведені карти поверхнево-потенційної енергії димерів уронатних полісахаридів та основні характеристики стійких конформерів високогулуронатного альгінату натрію та пектину низькоетерифікованого амідованого дозволяють у достатній мірі адекватно відобразити етапи формування реальних колоїдних розчинів у процесі золь-гель перетворення. Дослідження, що проводяться у даному напрямку мають вагоме значення для розробки способів керованої регуляції властивостей гелів на основі уронатних полісахаридів з елементами, що формують нанометричні структури. Результати роботи стали науковим підґрунтям для розробки технології харчових покриттів, що самоорганізуються за стадартних умов та біодеградують.

Ключові слова: уронатні полісахариди, гелеутворення, поверхнево-потенційна енергія, квантово-хімічне моделювання, конформери.

В статье рассмотрены важные аспекты компьютерного моделирования процессов, протекающих при образовании гелей пищевых пленкообразующих. Приведенные карты поверхностно-потенциальной энергии димеров уронатных полисахаридов и основные характеристики устойчивых конформеров высокогулуронатного альгината натрия и пектина низкоэтерифицированного амидированного в достаточной мере позволяют адекватно отразить этапы формирования реальных коллоидных растворов в процессе золь-гель превращения. Проводимые в данном направлении исследования, имеют большое значение для разработки способов управляемой регуляции свойств гелей на основе уронатных полисахаридов с элементами, формирующими нанометрические структуры. Результаты работы стали научным обоснованием разработки технологии пищевых, самоорганизующихся при стандартных условиях, и биодеградируемых покрытий.

Ключевые слова: уронатные полисахариды, гелеобразование, поверхностно-потенциальная энергия, квантово-химическое моделирование, конформеры.

In the article important aspects of computer modeling of the processes occurring during the formation of food film-forming gels are considered. The given maps of the surface potential energy of uroconate polysaccharides dimers and the main characteristics of stable conformers of high-guluronate sodium alginate and pectin of low-esterified amidated sufficiently allow adequately to reflect the stages of real colloidal solutions formation in the process of sol-gel conversion. The studies carried out in this direction are of great importance for the development of methods for controlled regulation of the properties of gels based on uroconate polysaccharides with elements forming nanometric structures. The results of the work became the scientific basis for the development of food self-organizing technology under standard conditions and biodegradable coatings.

Keywords: urogenital polysaccharides, gelling, surface-potential energy, quantum-chemical modeling, conformers.

Introduction

Nanoscale objects and objects of the macrocosm have substantial distinctions. The modern science experimental researches quite often become resource intensive and uneconomical making it impossible or very difficult to conduct a direct experiment.

In this case, the method of quantum-chemical modeling is irreplaceable and most accurate. The modeling process itself makes it possible to monitor the factors and understand the conditions creating the behavioral characteristics of the simulated environment and real objects. At the same time, the fact that modeling is based on the fundamental physical and chemical laws allows us to reveal the new features and capabilities of the system.

Quantum-chemical modeling of the processes of food film-forming gels formation will help to detail the characteristics of the researched objects participation in the process of creating gel systems and based on them biodegradable films; to study their properties at the molecular level and to build possible structures of polysaccharide matrices taking into account the action of the solvent. This problem is of scientific interest both for understanding the formation of gel systems on the basis of uroconate polysaccharides (sodium alginate and pectin) and the formation of films that can retain high organoleptic properties of the finished product for a long time and at the same time have the ability to biodegrade. Special attention was paid to determining the properties of the minimal structural units (dimers) that make up the system and possess its properties at the maximum. Their conformational analysis was carried out, geometry and thermodynamic characteristics were determined.

Stating the problem in general and its connection with the important scientific or practical tasks.

Computer modeling of nanoscale particles synthesis processes and their compositions is widely used for the detailed understanding of the nature of irregular processes of polymeric structures origin and growth. Quantum-chemical modeling of the reaction of ionotropic gelling with the involvement of sodium alginate [1] and pectin [2] was investigated earlier. The result was not only a more detailed study of the processes and gel net formation, but it also provided a deeper penetration into the phenomena that would be impossible to understand by means of traditional methods of analyzing these systems.

To date, the study of properties based on uroconate polysaccharides compositions is most relevant, since in the number of studies, strategically important for pharmacy and medicine effects of "cross-copolymerization" of these objects have been found [3–6]. It should be noted that the descriptions of the "pectin-alginate" system properties in the results of these studies are of a prognostic nature and do not explain the chemical nature of interaction between the components, do not describe the nature of binding of the structural elements in the system demonstrating only the dynamics of fixed indicators in time or their dependence on physical forces of impact.

The aim of this study is to create simulation models of the centres of binding polysaccharide chains between themselves and solvent molecules in the system of polymer composition between high-guluronate sodium alginate and pectin low-esterified amidated. One more goal of the work is to develop a methodology for computer modeling of the processes of nanoscale objects formation at the initial stages of chemical reactions, taking into account the interaction of the original components, their structural features and the parameters of technological processes.

To achieve the goals, the following tasks were formulated:

1. Investigation of the projected centers of nanoscale structures (dimers of maternity polysaccharides) formation at the initial stages of the gelling process;

2. Creation of a simulation model of the synthesized nanostructure during the "cross-copolymerization" of uronate polysaccharides molecules;

3. Development of a methodology for step-by-step modeling of nanostructures synthesis.

Presentation of the studies

In this paper, we present the results of quantum-chemical modeling of the conformational properties of alginate uronic acid dimers (Figure 1) and pectin (Figure 2.), taking into account the differences in alginate acid composition and presence of the ester and / or amide group in pectin.

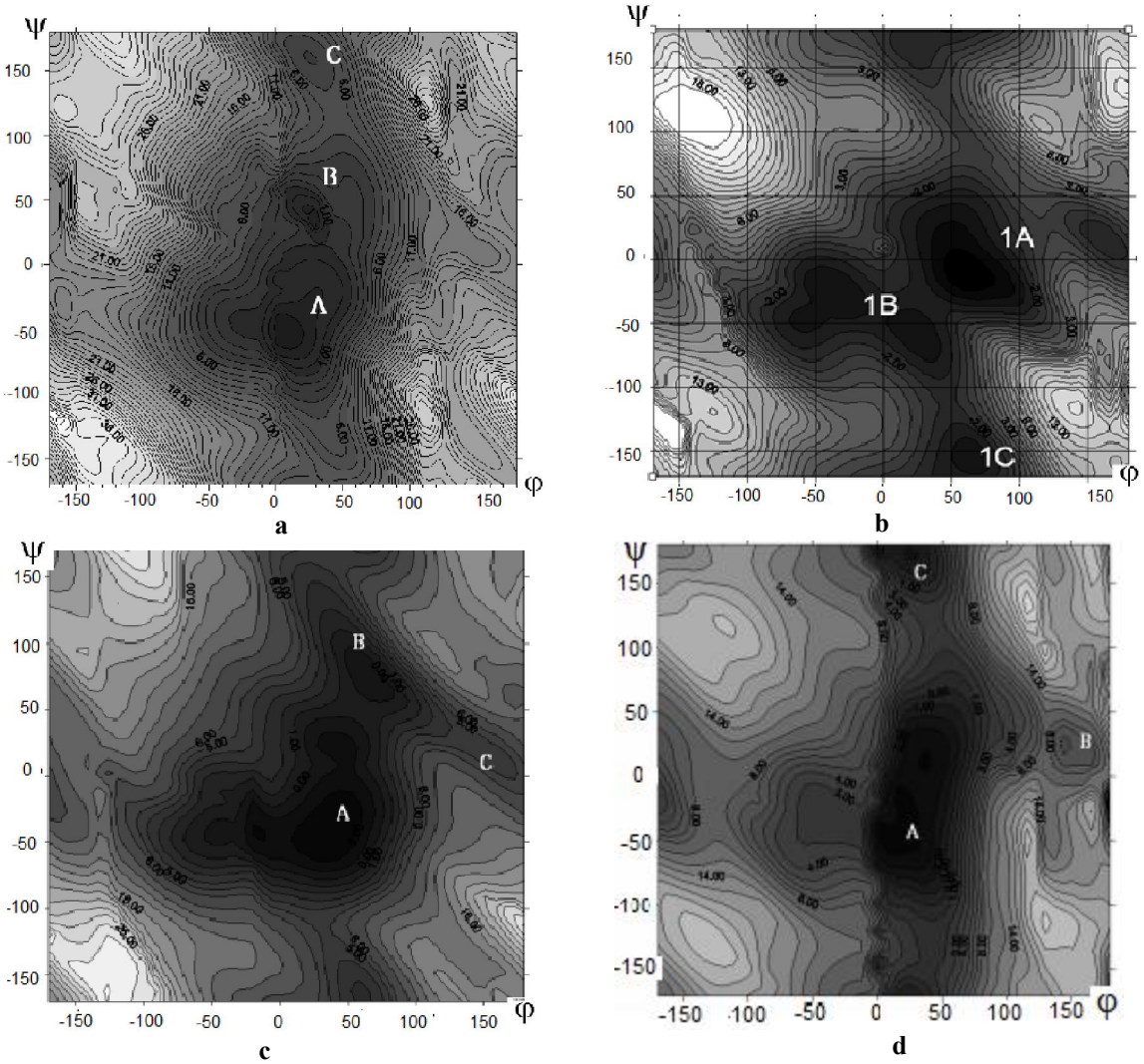

Fig 1. Contour maps of the potential energy surface for sodium alginate dimers:
a – guluronate-guluronate; b – mannuronate-mannuronate;
c – guluronate-mannuronate; d – mannuronate-guluronate

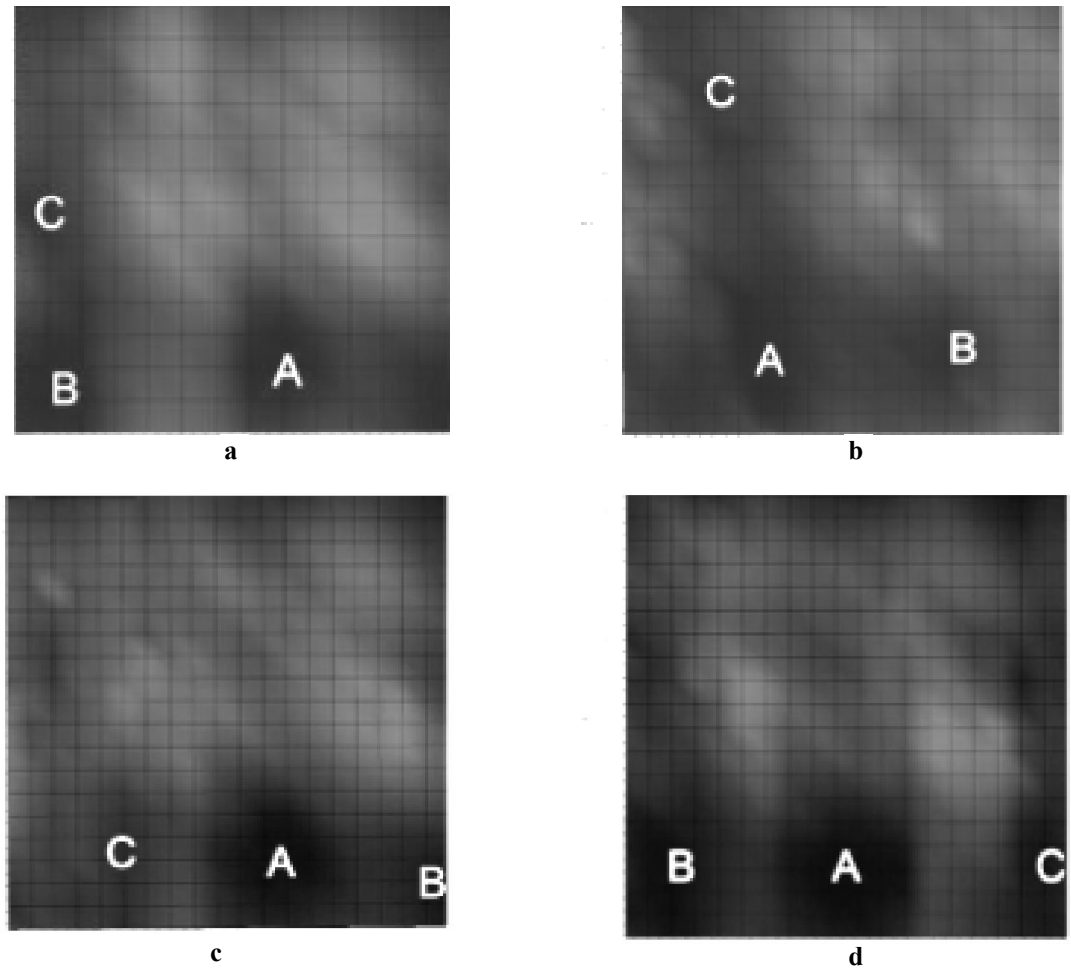

Fig 2. Contour maps of the potential energy surface for pectin dimers with groups next function groups: a – carboxyl-carboxyl; b – ester; c – amide; d - carboxyl-amide

Program Gaussian 09 [7] was used for calculations. To scan the potential energy surfaces regarding the torsion angles φ and ψ the PM3 method was applied [8]. The structure and energy of conformations corresponding to energy minima were refined by complete structures optimization. In so doing, possible ways of binding dimers into polymer chains of "sandwich type" for the subsequent "cross-copolymerization" with the participation of calcium ions were considered.

As shown in Fig. 1a, three regions (A, B, C) corresponding to stable conformers of the dimer-dimer "guluronate-guluronate" are clearly marked on the surface of the potential energy. For the complete presentation of the principle of complex interaction between dimers, and also in the case of the formation of cross-copolymer structures cross-linked by calcium ion, it is necessary to consider analogous systems with manuronate-manuronate, guluronate-manuronate, and manuronate-guluronate segments. The results shown in Fig. 1 b-g, describe in each investigated object three regions that indicate the existence of three stable conformers.

Similar tendencies were also observed in the structures of pectin dimers (Fig. 2a-d). Fig. 2 shows that on PPE maps of the examined objects, three regions with energy minima can be seen. All conformational transitions are characterized by low energy barriers - 8.2-26.6 kJ / mol. Other transitions are highly labile in the examined systems. This testifies to the sufficient flexibility of the conformer pairs and their easy transition to conformations, necessary for creating complexes with metal cations, directly with calcium ions.

On the basis of the results, describing the structural features of each examined polymers dimers, we proposed the theoretical model that recreates their direct interaction. The basis for constructing such a system can be the data of the experimental study of the ionotropic gelling process, according to which it is possible to affirm the existence of a "chemical" interaction between four groups -COOH (in various variations of pectin and alginate dimers) with a calcium ion (Fig.3).

From the technological point of view, this indicates that with the excess of calcium ions Ca^{2+} in the system it becomes possible to carry out all the transitions irrespective of the activation energy, and this affects the reduction in the number of hydrogen bonds and changes the structural and mechanical properties of the system. At reasoned concentrations of bi- or polyvalent metals, transitions occur only under the condition of energetically favorable pathways. This is the essence of system technological properties correction.

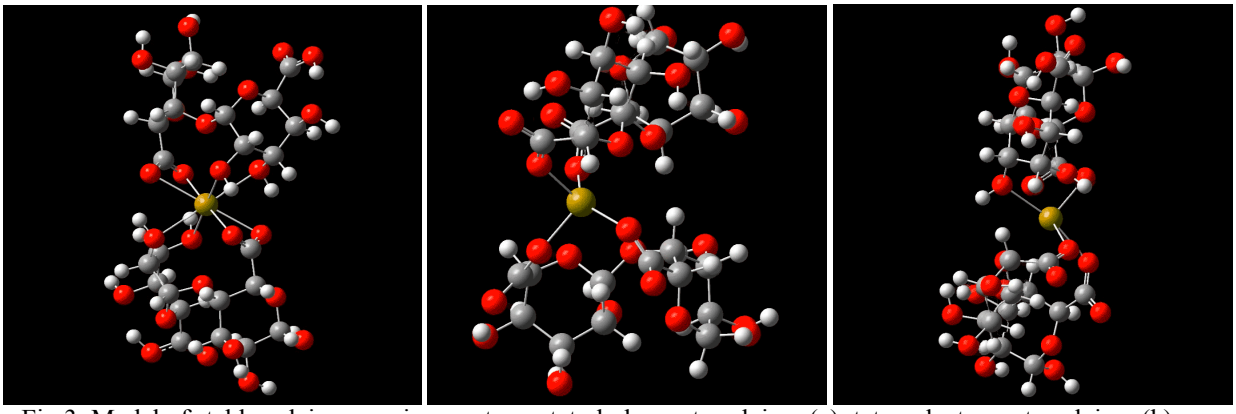

Fig 3. Model of stable calcium uranium systems: tetrahuluronate calcium (a); tetragalacturonate calcium (b); diguluronotadigalacturonate calcium (c).

Conclusions and prospects for this direction further development.

Thus, in this paper, the most energetically stable structures of the GG dimer, and the transition states of the corresponding conformational transitions are localized. The calculated dimensions of the activation barriers indicate the high conformational lability of the system.

The work describes the predicted centers of nanoscale structures (dimers of uroconate polysaccharides) formation at the initial stages of the gelling process. Such are tetrahuluronate, tetramanuronate, diguluronate dimanuronate, digmanuronate dihyluronate, tetragalacturonate, and diguluronad dihalacturonate structures.

Based on the obtained surface potential energy maps, simulated models of synthesized nanostructures were created during the "cross-copolymerization" of molecules of uroconate polysaccharides.

The given above stages of modeling became the basis of algorithm for the synthesis of nanostructures, described by the "alginate-pectin" gel system.

The proposed compositions in the form of hydrogels and films are economically most justifiable, since they definitely prevent the loss of the finished product's presentation and reduce the risk of contamination of the finished product surface by the pathogenic microorganisms.

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