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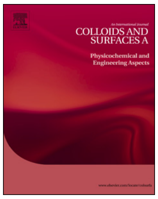

Quantum-chemical analysis of condensed monolayer phases of *N*-alkanoyl-substituted alanine at the air/water interface

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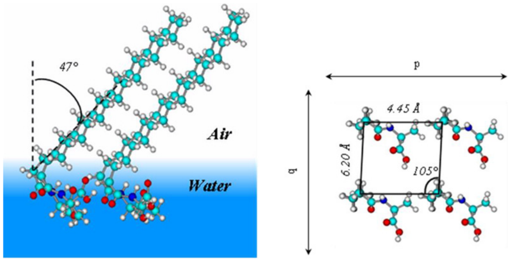
GRAPHICAL ABSTRACT

Clusterization process of *N*-alkanoyl-substituted alanine.



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ABSTRACT

The thermodynamic and structural parameters of monolayers of *N*-alkanoyl-substituted alanine with 8–17 methylene fragments in the alkyl chain are calculated on the basis of the quantum chemical semiempirical PM3 method. Four optimized structures of monomers are obtained. The energetically most preferred conformer is used for construction of dimers with “sequential” and “parallel” orientation of the hydrophilic parts of the monomers and tetramers with square structure. The hydrophobic chains of *N*-alkanoyl-substituted alanine are found to be inclined in the dimers to the normal of the spread monolayer: $\delta = 10°$ and $\varphi = 43°$.

Comparison of clusterization Gibbs' energy for small clusters suggests that 2D film formation takes place by formation of linear associates comprised of dimers with “parallel” orientation of the hydrophilic groups. The temperature increase causes growth of linear 1D clusters leading to the dendritic structure of the monolayer. The parameters of the unit cell of 2D film are calculated: $a = 4.65$ Å, $b = 6.20$ Å, the angle between the sides of the cell $\theta = 105°$. The tilt angle of amphiphilic molecules to the normal of the air/water interface is $t = 47°$. The calculated parameters of the unit cell are in good agreement with the existing experimental data. The spontaneous clusterization threshold for *N*-alkanoyl-substituted alanine at the air/water interface is calculated to be 15 carbon atoms in the chain at 288 K. This is only 2 carbon atoms more than the experimental value and within the margin of error of the model used for the calculation.

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1. Introduction

Biological membranes have amphiphilic nature and are generally composed of proteins with amino acids at the primary structural hierarchy, lipid molecules and carbohydrates. Because of the multifaceted membrane structure, monolayers are frequently used as model systems to understand the complicated physicochemical factors responsible for the mechanisms effective in the biological membranes. Amino acid-type amphiphiles have been of considerable interest both from the industrial and the domestic perspective caused by the good biodegradability and low toxicity [1].

Langmuir monolayers of *N*-alkanoyl-substituted α-amino acids have been traditional objects for experimental studies on mesoscopic and microscopic level using surface pressure–molecular area (Π-A) isotherms, Brewster angle microscopy (BAM), Grazing incidence X-ray diffraction (GIXD) and infrared reflection-absorption spectroscopy [2–9]. Rather strong attraction forces exist between the molecules of *N*-alkanoyl-substituted amino acid amphiphiles facilitated by hydrogen bonds. An essential advantage of *N*-alkanoyl-substitution in the amino acid amphiphiles is that possible effects of zwitter ion formation, as can be expected for amino acid monolayer, are prevented and can be excluded.

These monolayers are good candidates to study chiral discrimination effects that are demonstrated in various ways, such as shape and characteristic features of the Π-A isotherms, the domain morphology formed in the condensed phase, or differences in the lattice structures of the enantiomeric and racemic mixtures. The preference of homo or heterochiral interactions in racemic mixtures has been frequently discussed on the basis of experimental studies of *N*-alkanoyl-substituted amino acids [5,11–13] and their esters [3,10]. Previous analysis of surface pressure–area (Π-A) isotherms of numerous *N*-alkanoyl-substituted amphiphiles suggested homochiral or heterochiral monolayers [2–6], but the results concluded from thermodynamic results of isotherm measurements concerning the causing molecular interaction, must be thoroughly checked. The large variety of domain shapes obtained from different *N*-alkanoyl-substituted α-amino acid molecules, detected in BAM studies, presents a difficult task to receive some general deductions about the relationship of domain topography with the molecular structure [14].

Fundamental studies have been focused to comprehending the driving forces for the aggregation processes of amphiphilic monolayers [15]. First theoretical analyses of chiral discrimination and phase transitions in Langmuir monolayers are based on the “tripod model” of Andelman [16,17]. The ingenious stereogenicity at the chiral center of a molecule causes the chiral features, such as the specific curvature or handedness in the condensed phase domains of the monolayers. Another theoretical approaches based on the effective pair potential (EPP) and the intermolecular potential of a pair of chiral molecules between the interacting chiral amphiphiles [18,19] were applied to chiral amphiphiles containing headgroups of *N*-alkanoyl-substituted amino acids.

The objective of the present study is to calculate the thermodynamic and structural parameters of clusterization in finite and infinite clusters for *N*-alkanoyl-substituted alanine with n = 8–17 carbon atoms in the chain at the air/water interface in the frame of the quantum chemical semiempirical PM3 method to obtain new theoretical verification of the experimental results.

The results can be correlated to the main-phase transition of *N*-alkanoyl-substituted alanine at the air/water interface and their analysis indicates the possible way of the clusterization process.

2. Method

Structural and energetic parameters of clusterization for *N*-alkanoyl-substituted alanine were calculated using quantum chemical program package Mopac 2000 [20] utilizing the semiempiric PM3 method. A large number of papers deals with the nonempirical calculation of energy and length of the noncovalent CH···HC bonds only for dimers of short-chained hydrocarbons. The structure and ability to monolayer formation by amphiphilic compounds depends mainly on dispersion interactions between the alkyl chains (CH···HC interactions). Naturally, systems with such interactions should be examined using higher level *ab initio* or dispersion corrected density functional (DFT) methods. Calculations done only for small aggregates (dimers) with very short chain lengths will not enable to single out the necessary increments for the interactions between surfactant headgroups and alkyl chains using correlation analysis. This prevents the construction of the additive scheme for the description of large and infinite clusters. In the following, we compare the data concerning the length and energy of CH···HC bonds obtained by other more accurate methods in order to justify the results obtained using PM3 method.

The binding energies of typical van der Waals aggregates vary within the scope of several kilocalories per mole, while the intermolecular distance is more than 2 Å [21]. In the studies [22,23], dealing with the investigation of methane dimers in the framework of Møller–Plesset perturbation theory (MP2 calculations with the 6–311 G (2df,2pf) and 6–311 G (2d,2p) basis sets), the stabilizing effect of interactions between the methylene units of monomers is in the limit of 1.7 kJ/mol. The energetic effect of methane and ethylene dimerization was calculated to be −2.22 and −6.31 kJ/mol [24,25] using the coupled cluster method covering single, double, and triple excitations iteratively (CCSD(T)). These values are in good agreement with data of Monteiro and Firme [26] for dimers of C_nH_{2n+2} (n = 1–6): −(0.84–22.57) kJ/mol calculated at ωB97XD/6-311 + +G(d,p) level of theory. Thus, for one CH···HC interaction it makes –(0.84–2.82) kJ/mol. The length of the CH···HC bonds assessed in this investigation is in range of 2.3–2.6 Å. In the study of Ref. [27]. CH···HC interactions were classified as weak van der Waals interactions in terms of the first four criteria proposed by Koch and Popelier. Matta et al. [28] assessed the energy of these interactions in the range of −(3.3–16.7) kJ/mol using B3LYP 6-31G** calculations. The mentioned energy values agree well with those obtained in the framework of PM3 method: −(2.81 − 4.93) kJ/mol per one CH···HC interaction [29]. The later PM6 and PM7 parametrizations give −9.20 and −4.18 kJ/mol per one CH···HC bond, respectively.

A*b initio* calculations [30] concerning the length of CH···HC bonds offer the following results: 2.167–2.992 Å for intermolecular and 1.976–1.985 Å for intramolecular CH···HC bonds. The authors of the Ref. [26] present the length of 2.358–2.521 Å for intermolecular CH···HC bonds. Calculation of the structures of the methane dimers using MP2 with BSSE correction and 6–311 + +G(3df,3pd) basic set gives the next results for dissociation energy: 052–1,6 kJ/mol depending on the dimer topology. The length of the CH···HC bonds is 2.50–3.03 Å [31]. The length of the CH···HC bonds in the polyhedrane dimers is 2.114–3.197 Å obtained by Echeverria and coworkers in the frameworks of MP2 and MP4 method [32]. The mentioned values are higher than the length of CH···HC bonds assessed in the framework the semiempirical PM3 method (1.7–1.8 Å) [33] for interacting surfactants. It should be stated that there are extremely short CH···HC bonds with length of 1.73 Å for fullerene dimer, 32 1.126 Å for $C_{59}H_{56}$ [34] that is shorter than the previously detected minimum 1.566 Å for (3,5-*tert*-butylphenyl)methane [35]. The authors of Ref. [36] analized the performance of different semiempirical methods. They showed that newer PM6 and PM7 methods understate the length of CH···HC bond as 1.7 and 1.5 Å, respectively. These values are by 0.3–0.5 Å shorter than those assessed by the MP2 method. However, it also overestimates the dispersion interactions [37]. The authors of Ref. [38] calculated the distance between the molecular chains of interacting *n*-alkanes with 3.96–4.09 Å using DFT. It is simple to assess the length of CH···HC bonds (1.78–1.91 Å) supposing the length of C−H bonds. Although, there are studies which show that the PM3 method overestimate the attraction forces between hydrocarbon chains [39], still it satisfactorily reproduces the values of the geometric parameters of the unit cells for the monolayers of nonionic surfactants studied in our previous papers [40–48]. The agreement of calculated and experimental data [49–56] allows us to use the PM3 method to describe the thermodynamic and