



A simple method for estimation of the 2D cluster formation temperature of substituted alkanes at the air/water interface

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ARTICLE INFO

Article history:

Received 22 September 2011

Received in revised form 8 March 2012

Accepted 19 March 2012

Available online 7 April 2012

Keywords:

Quantum chemical semiempiric PM3 method

Thermodynamic parameters

Amphiphilic compounds

Clusterization

ABSTRACT

A simple method for estimation of the 2D spontaneous clusterization temperature of substituted alkanes at the air/water interface versus alkyl chain length is proposed using the quantum chemical semiempirical PM3 method. The method is approved by long-chain amines, alcohols, thioalcohols, saturated and unsaturated carboxylic acids, α -amino acids and amides of carboxylic acids.

The method is based on the experimental fact that short chain amphiphilic molecules cannot form condensed 2D monolayers whereas above a specific alkyl chain length condensed monolayer phases can be observed under the same conditions. That is, elongation of the alkyl chain of amphiphilic molecules causes the increase of intermolecular interaction energy between them what stimulates their close packing and structuring. This leads to linear or stepwise dependencies of enthalpy and entropy of cluster formation on the alkyl chain length. It is possible to obtain an equation for the estimation of the temperature of the spontaneous clusterization threshold of the considered substituted alkane types by setting Gibbs' energy equal to zero and by knowing the regression expressions for determination of enthalpy and entropy of cluster formation calculated under the condition of 298 K using coefficients which determine the contribution of the hydrophilic head group interactions of molecules and $\text{CH}\cdots\text{HC}$ -interactions between the alkyl chains.

It is shown that the temperature dependence of the spontaneous clusterization threshold on the alkyl chain length of the amphiphile is fractionally linear with a relative error of 3–8%. The effect of the alkyl chain elongation of substituted alkanes by two methylene units corresponds to subphase temperature reduction (ΔT) by 10–20 K in good agreement with the available experimental data. The difference between ΔT values for considered types of amphiphilic compounds becomes less significant with the lengthening of the alkyl chain. This indicates the basic contribution of intermolecular $\text{CH}\cdots\text{HC}$ -interactions between the alkyl chains to the process of the 2D clusterization.

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Langmuir monolayers at the air–water interface have successfully been used as simple models to develop tailor-made functional nanomaterials and to mimic biological phenomena. Significant progress is made toward the understanding of the model systems [1,2]. Supramolecular architecture systems with new properties and functions have been successfully designed by specific composition of two or more various molecular components [3–5]. A further target for such model studies is to transfer the obtained knowledge to biological systems where fundamental physical principles are operative in the same way [6]. Langmuir monolayers are the basis for the well-established LB technique [7,8] proposed recently for producing ultra thin self-assembled molecular coatings with

controllable interfacial molecular orientation and mesostructured features [9,10].

Models have been developed that enable the assessment of the thermodynamic parameters for clusterization of amphiphilic monolayers in order to obtain information about the process of the structure formation during the fluid/condensed phase transition of the monolayer.

It was the objective of the present work to introduce a simple method for the estimation of the 2D spontaneous clusterization temperature of substituted alkanes at the air/water interface using the quantum chemical semiempirical PM3 method.

Therefore, the possibility of condensed 2D films formation for different types of substituted alkanes without carrying out experimental studies should be estimated. We used the previously calculated values of enthalpy and entropy of cluster formation of amines, alcohols, thioalcohols, saturated and unsaturated fatty

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