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

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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 CH···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 CH···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 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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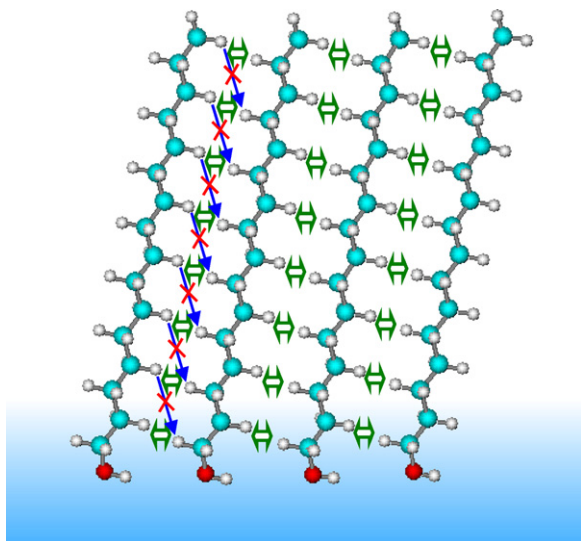
Fig. 1. Schematic notion of the intermolecular CH⋯HC interactions realized between alkyl chains of amphiphilic molecules in the monolayer. (For interpretation of the references to color in this text, the reader is referred to the web version of this article.)

acids, α-amino acids and amides of fatty acids at the air/water interface [11–16] in the frameworks of the quantum-chemical semiempirical PM3 method [17]. This method is used because of its parameterization with respect to the formation heats [18,19] and inclusion of atom–atom potentials that, despite some restrictions [20], allows an appropriate definition of van der Waals' interactions. Therefore this method is capable of the interpretation of experimental data concerning monolayer formation of different types of substituted alkanes.

The calculation of the thermodynamic parameters of cluster formation of mentioned types of amphiphiles [11–16] was carried out according to the model on the basis of the following key points:

- the intermolecular CH⋯HC interactions between the methylene groups of alkyl chains of interacting amphiphiphile molecules provide the main contribution to the Gibbs' energy of cluster formation;
- the calculation of the thermodynamic parameters of the cluster formation of considered types of amphiphiles was carried out in the supermolecule approximation;
- the additive scheme was constructed on the basis of the results of direct calculations. This scheme defines the values of the thermodynamic parameters of clusterization as the total contribution of the CH⋯HC interactions and the interactions of hydrophilic part of the amphiphile molecules realized in the cluster;
- as demonstrated in Fig. 1, only the CH⋯HC interactions realized between two methylene groups of the alkyl chains arranged opposite to each other (marked with the green arrow) are taken into account and the interactions between alkyl groups arranged much farther (marked with crossed blue arrow) are neglected because of the decrease of interaction energy inversely proportional to the r^6, i.e. the CH⋯HC interactions are additive in pairs;
- the coefficients finding in the frameworks of additive scheme were used to obtain the thermodynamic parameter values of the cluster formation of large associates including 2D monolayers.

According to this model the values of enthalpy and entropy of cluster formation of dimers, trimers and larger clusters up to infinite 2D monolayers can be defined in the following way:

$$\Delta H_{(T)}^{Cl} = i \cdot n_f + j \cdot K_a, \quad \Delta S_{(T)}^{Cl} = k \cdot n_f + l \cdot K_a. \quad (1)$$

Here, K_a is the number of the 'a' CH⋯HC interactions type realized in the cluster. It depends on the number of methylene fragments (n) in the alkyl chain and the structural features of the considered clusters. The K_a value is calculated according to the equations given in [11–16], i and k are the coefficients that define the contributions of interactions between the hydrophilic parts of interacting amphiphile molecules (the number of these interactions are equal to n_f) in the enthalpy and entropy of cluster formation, respectively, j and l are the coefficients that define the contributions of the intermolecular CH⋯HC interactions between the alkyl chains of amphiphilic compounds in the enthalpy and entropy of cluster formation, respectively. The values of the regression coefficients that enter into the expressions for the calculation of enthalpy and entropy of clusterization per one monomer for all considered types of amphiphilic compounds at the temperature 298 K are listed in Table 1.

For the calculation of the temperature of the spontaneous cluster formation threshold of surfactants (T) the equation for definition of the Gibbs' energy of cluster formation is used:

$$\Delta G_{(T),\infty}^{Cl} = \Delta H_{(T),\infty}^{Cl} - T \cdot \Delta S_{(T),\infty}^{Cl} = i + j \cdot K_a - T(k + l \cdot K_a). \quad (2)$$

From this expression if $\Delta G_{(T),\infty}^{Cl}$ is taken as zero, it is easy to get the equation for the temperature of the spontaneous cluster formation as the ratio of the enthalpy to the entropy of cluster formation including the corresponding thermodynamic properties of cluster formation per monomer of the infinite 2D films:

$$T = \frac{i + j \cdot K_a}{k + l \cdot K_a}, \quad (3)$$

where the coefficients i, j, k and l have the same meaning as in Eq. (2), their values calculated at 298 K are listed in Table 1, and K_a is the number of the intermolecular CH⋯HC interactions per one monomer of the infinite 2D clusters of the considered types of substituted alkanes.

It should be noted that the values of the coefficients i, j, k and l depend on the temperature and there are a few approaches to take this dependence into account which differ from each other by the degree of their theoretical validity. The main idea of scheme 1 is the use of the temperature dependencies of enthalpy and entropy of clusterization of the small associates (dimers, tetramers, hexamers) determined by using the expansion coefficients of the heat capacity (a, b, c'). Note that values of ΔH_{298}^{Cl}, ΔS_{298}^{Cl}, a, b and c' should be factorized contributions of the hydrophilic head groups and the CH⋯HC interactions between the alkyl chains of the interacting molecules. Then, the terms T, T^2, T^3, $T \ln T$, $K_a T$, $K_a T^2$ and $K_a T \ln T$ can be inserted into the formula for calculating ΔG_{298}^{Cl}. Due to the lack of reference data for the values of the expansion coefficients of the heat capacity (a, b, c') it is impossible to exploit this scheme. Therefore, the simplification of scheme 1 can be implemented in different ways: corresponding variables T, T^2, T^3, $T \ln T$, $K_a T$, $K_a T^2$ and $K_a T \ln T$ as constants are found by linear regression using all temperature data array available for ΔG_{298}^{Cl} (scheme 2); by linear regression for enthalpy and entropy of clusterization at each of the considered temperatures (scheme 3); neglecting the dependence of the coefficients of enthalpy and entropy of clusterization on the temperature and using the values of these coefficients found for one of the temperature values, e.g. 298 K (scheme 4).

In the present work we regard the simplest and consequently the roughest approach in detail. In this scheme the values of the coefficients i, j, k and l are taken from the correlation expressions for the enthalpy and the entropy of clusterization calculated at one definite temperature value (e.g., 298 K, cf. Table 1). That is, we consider the dependency of the values of the coefficients i, j, k and l on the temperature in Eq. (3) as negligible. It can be done if the process of the cluster formation is carried out in a narrow temperature