Temperature Effects on the Monolayer Formation of Substituted Alkanes at the Air/Water Interface Estimated in the Frameworks of the PM3 Method

Yu.B. Vysotsky\textsuperscript{1}, E.S. Fomina\textsuperscript{1}, D. Vollhardt\textsuperscript{2} and R. Miller\textsuperscript{2}

\textsuperscript{1}Donetsk National Technical University, 58 Artema Str., 83000 Donetsk, Ukraine,
\textsuperscript{2}Max Planck Institute of Colloids and Interfaces, D-14424 Potsdam/Golm, Germany

The approach of calculation of the threshold temperature of spontaneous clusterization of substituted alkanes (amines, alcohols, thioalcohols, saturated and unsaturated carboxylic acids, α-amino acids, amides of carboxylic acids and melamine) at the air/water interface versus the alkyl chain length was developed using the semi-empirical quantum chemical method PM3. In the framework of this approach four schemes for calculation of the thermodynamic parameters of clusterization were developed 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 using the expansion coefficients of heat capacity \((a, b, c')\). Note that the values of \(\Delta H_{298}^{CI}, \Delta S_{298}^{CI}, a, b\) and \(c'\) should be factorized contributions of interacting hydrophilic ‘heads’ and CH–···HC interactions between alkyl chains of interacting molecules. Then, the terms \(T, T^2, T^3, TlnT, K_aT, K_aT^2\) and \(K_aTlnT\) can be inserted into the formula for calculating \(\Delta G_{298}^{CI}\). Due to lack of reference data for values of the expansion coefficients of the heat capacity \((a, b, c')\) it is impossible to exploit this scheme. Therefore, a simplification of scheme 1 can be implemented in different ways: the corresponding variables \(T, T^2, T^3, TlnT, K_aT, K_aT^2\) and \(K_aTlnT\) as constants are found via linear regression over available temperature data (278 K, 298 K, 318 K) for \(\Delta G_{298}^{CI}\) (scheme 2); via linear regression of the enthalpy and entropy of clusterization at each of the considered temperatures (scheme 3); neglecting the dependence of the coefficients for calculating the enthalpy and entropy of clusterization on temperature and using the values of these coefficients found for one of the temperature values 278 K, 298 K or 318 K (scheme 4).

With the proposed schemes one can calculate the threshold temperature \(T\) of spontaneous clusterization of substituted alkanes and the variation increment of this threshold temperature \(\Delta T\) with the alkyl chain length (cf. Figure on the example of α-amino acids). The accuracy of calculations of \(T\) and \(\Delta T\) decreases from the second to the fourth scheme due to more theoretical simplification. However, taking into account the detected systematic error (3.6±0.8) K allows calculating the \(\Delta T\) values sufficiently accurately ±0.6 K even using the roughest scheme 4. Thus the ‘temperature effect’ according to which the addition of two CH\(_2\) units to the alkyl chain has an effect similar to reducing the temperature of the spontaneous cluster formation by 10–20 K are similar for different classes of amphiphilic compounds. This finding agrees well with present experimental data.