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Subphase pH effect on the limiting molecular area of amphiphilic β-diketones in Langmuir monolayers

Julia M. Devterova, Mikhail E. Sokolov, Vladimir Yu. Buz'ko, Irina N. Repina, Peter S. Rudnov and Victor T. Panyushkin

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Experimental part

The surface pressure-area (π-A) isotherms

Measurement of surface pressure-area (π-A) isotherms was carried out using a polytetrafluoroethylene (PTFE)-coated KSV Minitrough II LB device (KSV Instruments, Finland) equipped with two polyacetal-made barriers for symmetric compression and a platinum Wilhelmy plate connected to a micro-electronic feedback for surface pressure measurement. The required volume of chloroform (purity 99.9%) solution of the β-diketone was gently applied dropwise on the surface of aqueous subphase by microsyringe (Hamilton, USA). The volume and concentration of the applied solutions were selected experimentally to start compression from gaseous state of the monolayer. After 15 min of chloroform evaporating, the monolayer was compressed at the constant rate of 10 mm/min and the isotherm was recorded of surface pressure (π) versus area per molecule (A). All experiments were performed at (25.0 ± 0.1) °C. The temperature of the subphase was maintained constant with a Julabo ED-5 recirculating thermostat (JULABO Labortechnik GmbH, Germany). All procedures were carried out in a dust-free box and the experiments were repeated at least twice.

Deionized water for the subphase (resistivity >18 MΩ·cm^{-1}) was prepared using "Aquarius" water deionizer (Russia). The pH values of the subphases were adjusted by addition of concentrated HCl or NaOH solutions; no buffer solutions were used.

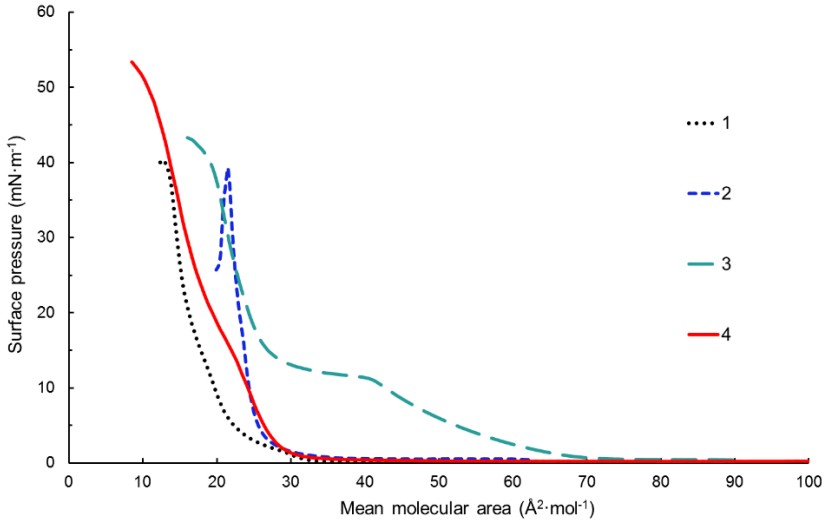

Figure S1 π-A compression isotherms of amphiphilic β-diketones **1**–**4** at subphase pH~7.

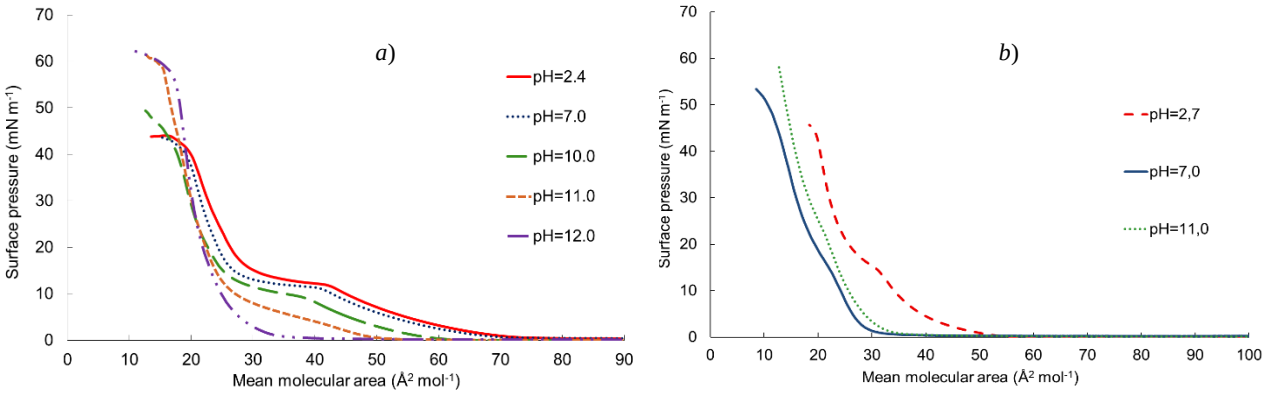

Figure S2 π-A compression isotherms of amphiphilic β-diketones (*a*) **3** and (*b*) **4** on aqueous subphases at different pH values.

Theoretical calculations

The theoretical limiting area ($A_{0(calc)}$) for the investigated β-diketone molecules in the molecular layer was calculated based on the hypothesis of the energetically stable hydration shells formation for surfactant molecules.

The energy dependence of the sequential hydration of an individual molecule of the studied β-diketones, surrounded by a different number of water molecules located in the space surrounding the diketonate structural fragment, was determined using molecular mechanics calculations by means MM + force field approximation (Figure S4). All calculations for the studied model clusters of β-diketones and water molecules were performed using the HyperChem 8.0.10 software package. Full molecular geometry optimizations for the investigated clusters for each structure from one molecule of the studied β-diketones and several water molecules located randomly around the diketonate fragment were carried out by the Pollack-Rieber conjugate gradient method to achieve an optimization limit of 0.005 kcal·mol^{-1} without any restrictions on symmetry or structural characteristics. From 6 to 10 different structures with different relative positions of water molecules surrounding β-diketone given randomly, were calculated independently for each hydrate from one molecule of the studied β-diketone and several water molecules. The most energetically favorable structures energies of their hydrates were taken to construct the dependence of the studied β-diketones molecule sequential hydration energy. Based on the graph construction of the sequential hydration energy dependence normalized to the hydration water molecules number, we determined the region of the stable first hydration shell with an observed minimum energy between 6 and 12 water molecules. The structure of one molecule of the studied β-diketone and several water molecules with the lowest sequential solvation energy from this region was used to calculate the hydrate molecular volume $V_{hydr.}$ using the specialized QSAR utility software package HyperChem 8.0.10. The molecular volume calculating method was also used to calculate the studied optimized β-diketone molecule volume $V_{diketone}$ without a hydration shell. The difference between the $V_{hydr.}$–$V_{diketone}$ allowed us

to estimate the molecular volume occupied by the group of water molecules bound by hydrogen bonds. The estimated limiting area $A_{0(calc)}$ for the studied β-diketone was determined based on the water molecules close packing approximation in the water sublayer under the monomolecular layers of surfactants. Then $A_{0(calc)} \approx (V_{hydr} - V_{diketone})_{2/3}$. The described approach is fundamentally different from the previously used approach for calculating $A_{0(calc)}$, which we described earlier in work,[S1] but gives similar results $A_{0\ (calculation)}$ with much less computational time and efforts.

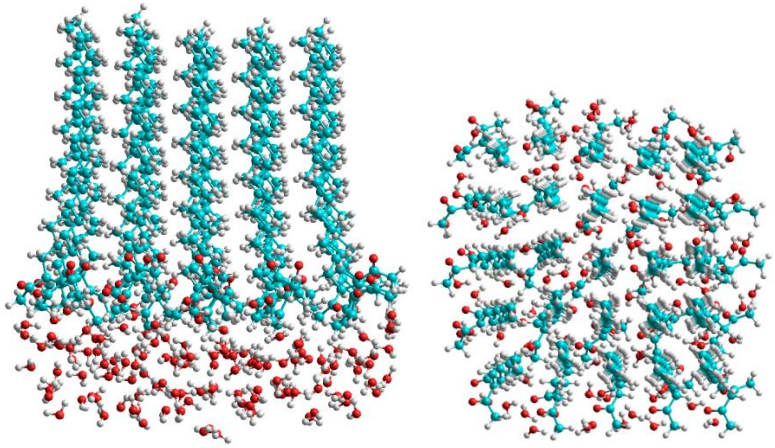

Figure S3 Projections of the structure of the Langmuir model monolayer for the studied β-diketone **2**.

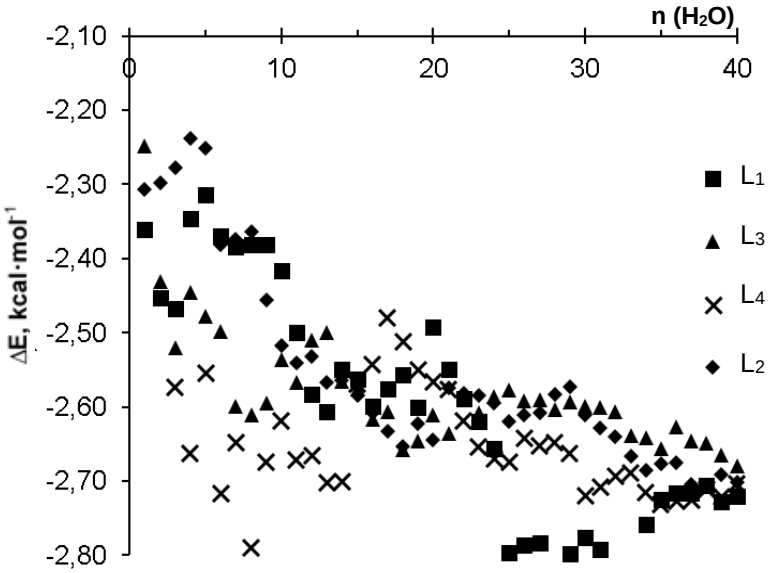

Figure S4 Energy dependence of the sequential hydration of an individual β-diketone molecule.

References

S1. Y. Buz'ko, G. Y. Chuiko, M. E. Sokolov and V. T. Panyushkin, *Russ. J. Phys. Chem. A.*, 2017, **91**, 2409.