EFFECT OF THE MONOLAYER FORMATION ON THE pK_a OF CARBOXYLIC ACIDS AT THE AIR/WATER INTERFACE WITHIN QUANTUM CHEMICAL APPROACH

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Acid-base properties of a substance are crucial in biology, organic synthesis, etc. The ionization degree of a compound affects its solubility in various media, which is especially important for studying its behavior at different interfaces. Computational methods have also been added to experimental ones for estimation of the acidity index (pKa) with the development of modern computers and computational algorithms.

The purpose of this work was to identify the dependence of the dissociation constant of monolayers for saturated carboxylic acids $C_nH_{2n+1}COOH$ (n=6-16) and their perfluorinated counterparts at the air/water interface on their chain length using a quantum chemical approach developed and successfully tested earlier when describing the film formation of more than ten classes of nonionic surfactants. The proposed model includes the calculation of the Gibbs energies of acid formation and dimerization in neutral and ionized forms, as well as the corresponding monomers, in the aqueous and gaseous phases. The approach does not require the construction of any thermodynamic cycles. The calculations were performed using semi-empirical quantum chemical methods PM3 and PM6 within the frameworks of the conductor-like screening model COSMO.

It is shown that the minimum Gibbs energy of clusterization corresponds to associates with the degree of dissociation α=0.5. A relationship has been derived between the values of surface and bulk pK_a. It follows that, unlike the bulk pK_a, the value of the surface pK_a depends on the surfactant chain length, which is due to the difference in the solvation energy of the hydrocarbon tails of the corresponding neutral and dissociated monomer. Thus, the calculated data showed that the elongation of the carboxylic acid chain by one CH_2 fragment leads to an increase in the surface pK_a by 0.43 units, and by 0.50 per CF_2 for perfluorinated ones. The obtained results are in good agreement with the available experimental data. [1, 2].

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2. Kartashynska E. S. Clustering Impact on the Acidity of Perfluorinated Carboxylic Acids at the Air/Water Interface Assessed within Semiempirical Quantum Chemical Approach // Theor. Chem. Acc. 2026. Vol. 145, Nr. 4. P. 35. https://doi.org/10.1007/s00214-026-03285-x

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