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

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Theoretical and experimental limiting molecular area values for a series of amphiphilic α- and γ-substituted β-diketones have been analyzed and compared. The investigated β-diketones exist in Langmuir monolayers as mixtures of keto and enol tautomeric forms. The ratio of the forms depends on the subphase pH and affects the shape of surface pressure–area isotherm and the experimentally determined limiting molecular area value for the monolayer.
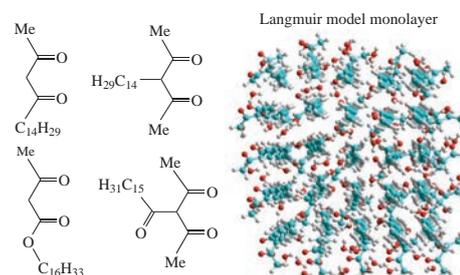
Keywords: Langmuir monolayer, amphiphilic β-diketones, keto-enol tautomerism, tautomeric forms, limiting molecular area, compression isotherm, theoretical calculations.

Amphiphilic β-diketones and related compounds as well as their complexes with ions of *d*- and *f*-elements possess valuable electronic, optical, magnetic and chemical properties and can be considered as promising molecular systems for the preparation of Langmuir–Blodgett films (LBFs) employed in micro- and nanoelectronics, optoelectronics, thin-film sensors and other multifunctional devices.[1–11] It has been shown for this type of compounds that both the shape of pressure–area (π–A) compression isotherms of Langmuir films and conditions for the LBF transfer strongly depend on the parameters of aqueous subphase, namely pH and concentration of metal ions.[12–15] It has been assumed that this relationship originates from equilibrium processes of keto-enol tautomerism and complexation, which influence the ratio of tautomeric forms for coordination compounds in the Langmuir molecular layer.

To verify this hypothesis, in this work the experimental limiting molecular areas were compared with theoretical ones for keto and enol forms of octadecane-2,4-dione **1**, 3-tetradecylpentane-2,4-dione **2**, hexadecyl 3-oxobutanoate **3** and 3-palmitoylpentane-2,4-dione **4**. These β-diketones with hydrophobic long-chain alkyl

substituents at the α- and γ-positions were synthesized by known methods.[15–18]
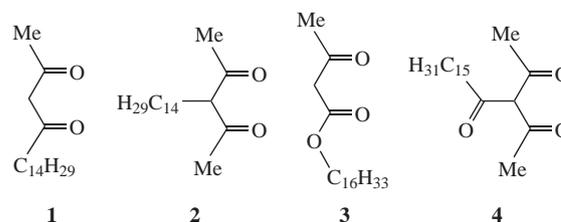
The values of limiting molecular area A_0 and the surface pressure value π_0 at a collapse point are considered as the main numerical characteristics in investigation of the subphase pH influence on the structural characteristics of β-diketones in Langmuir layer. The experimental values $A_{0(exp)}$ were determined from the π–A isotherms recorded at different pH of aqueous subphase (see Online Supplementary Materials) by extrapolating the slope of isotherm in its steepest range to the zero surface

Table 1 Theoretical and experimental values of limiting molecular area for amphiphilic β-diketones **1–4** at different subphase pH values.

β-diketone	$A_{0(calc)}$/Å² mol⁻¹		$A_{0(exp)}$/Å² mol⁻¹ pH											
	ketone	enol	1	2	3	4	5	6	7	8	9	10	11	12
1	23.81	23.78		20.5				21.3	20.7					20.6
2	34.05	18.99			25.5			24.5			25.5			
3	26.02	32.15	29.7	30.8	28.9	29.0	31.6	27.4	27.8	31.9	30.4	26.0	24.8	23.1
4	23.76	28.14		27.0		27.0	28.0	27.5	32.0	35.0	33.0		32.0	
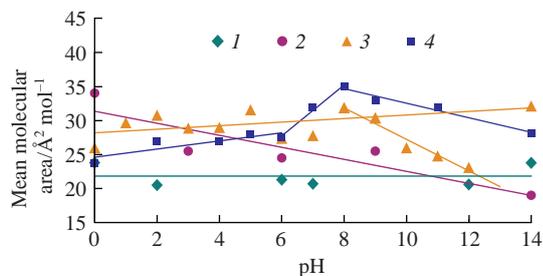
Figure 1 Values of limiting molecular area for amphiphilic β-diketones (*1*)–(*4*) **1**–**4**, respectively, on aqueous subphase at different pH. Theoretical values are located at pH 0 and 14 for keto and enol forms, respectively.

pressure. Then the theoretical values $A_{0(calc)}$ for the keto and enol forms were calculated by semiempirical method based on the assumption of formation of the energetically stable hydration shells for surfactant molecules (see Online Supplementary Materials). The resulting values of $A_{0(exp)}$ and $A_{0(calc)}$ are given in Table 1 and Figure 1.

As follows from the data obtained, for all the compounds except diketone **1**, the $A_{0(calc)}$ values for keto and enol forms differ considerably. Moreover, the experimental values at different pH vary uniformly within the range of theoretical data (see Table 1 and Figure 1). The dependencies for compounds **1** and **2** are linear. The absence of significant changes in the $A_{0(exp)}$ and $A_{0(calc)}$ values for compound **1** bearing a hydrophobic side substituent can be explained by similar geometrical parameters of both tautomeric forms. For compound **2** with a substituent in the α-position, $A_{0(calc)}$ values for keto and enol forms differ by ~15 $\text{Å}^2 \text{ mol}^{-1}$, which indicates the strong difference in the geometry of these forms. The experimental values for diketone **2** lie between the $A_{0(calc)}$ values for keto and enol forms and demonstrate nearly linear dependence on pH. This may imply that the experimental values result from tautomeric equilibrium in the molecular layer at a given pH. For compound **3**, a decrease in the $A_{0(exp)}$ values at pH > 8 indicates ester hydrolysis, however at lower pH the $A_{0(exp)}$ values approach the one for enol. Thus, the LBF of compound **3** is formed at pH < 8. For compound **4**, the shape of the dependence may reveal the presence of some intermediate structure with a larger area value at pH > 6, its concentration reaches maximum at pH 8 and gradually decreases to the value calculated for the enol form with further increase in pH followed by the predominance of enol. However, this assumption requires further exploration.

In summary, it can be concluded that amphiphilic β-diketones in Langmuir monolayers can exist in different forms with various structural parameters of their hydrophilic part, depending on the subphase pH. The distinction in molecular structure and properties of tautomeric forms can significantly affect the shape of π–A isotherms, the limiting molecular areas at different pH values of aqueous subphase and finally the conditions required for the monolayer transfer to substrate. In this regard, the preparation of LBFs based on amphiphilic β-diketones in specified tautomeric form should be controlled and maintained by the appropriate subphase pH value.

Online Supplementary Materials

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