

# Theoretical Description of Mixed Film Formation at the Air/Water Interface: Carboxylic Acids–Alcohols

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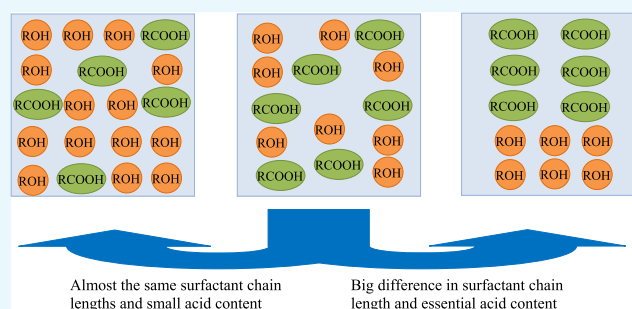
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**ABSTRACT:** The thermodynamic parameters of formation and clusterization of aliphatic alcohols  $C_nH_{2n+1}OH$  and carboxylic acids  $C_nH_{2n+1}COOH$  ( $n = 6–16$ ) are calculated using the quantum-chemical semiempirical PM3 method. Four types of dimers are constructed in two directions of the spread monolayer comprising the most energetically advantageous monomer structures. The hydrophobic chains of alcohol and carboxylic acid molecules in the regarded dimers are found to be tilted within  $12^\circ$  to the normal of the spread monolayer. The structures of the mixed and pure surfactant dimers are the basis for the mixed alcohol–carboxylic acid monolayers of the following types: two dimensional (2D) film 1 with single distribution of the individual component in the other one, when the molecules of the first component do not interact with each other but are completely surrounded by the molecules of the second component; 2D film 2 with domain structure, when the film consists of “islands” of the individual components. The dependences of the clusterization Gibbs’ energy per one monolayer molecule on the molar fraction of the components for the mixed 2D films 1 formed by surfactants with equal alkyl chain length are found to be limited from top to bottom by the corresponding dependences for pure components. This indicates the absence of synergetic interaction between the hydrophilic head groups of carboxylic acids and alcohols and conforms to the available experimental data. The formation of the described types of mixed films is competitive. The preferential formation of 2D films 1 with single distribution of the first component among the molecules of the second one is possible when the length of the carboxylic acid hydrocarbon chain is longer by  $\Delta n = 1–2$  methylene units than that of the corresponding alcohol alkyl chain. According to the fractionally linear law, the highest possible content of the carboxylic acids in such 2D films 1 depends on the  $\Delta n$  value and does not exceed 33.3%.



## INTRODUCTION

Although Langmuir monolayers have been studied since more than a century, they are of current and growing interest for offering unique information about the organization of molecules in the two-dimensional (2D) environment at the air/liquid interface.

The number of publications per year has grown exponentially with the development of new experimental techniques and is furthermore on a high level, indicating the general interest in the advantages of obtaining detailed information by model studies for more complex systems.<sup>1</sup>

The development of novel in situ methods at the air/liquid interface, such as Brewster angle microscopy,<sup>2–4</sup> grazing incidence X-ray diffraction,<sup>5,6</sup> infrared reflection absorption spectroscopy,<sup>7</sup> and surface selective sum frequency generation,<sup>8</sup> contributed decisively to the experimental progress. Besides the enormous number of monolayer studies of single amphiphiles, experimental investigations of two-component

systems concern mainly mixtures of nonionic amphiphiles (aliphatic alcohols, carboxylic acids, and so on) with ionic,<sup>9,10</sup> zwitter-ionic,<sup>11,12</sup> and aromatic<sup>13</sup> compounds. Essentially, less papers deal with monolayer formation of nonionic surfactant mixtures, for example, discussing the peculiarities of monolayers of fatty alcohol–carboxylic acid<sup>14</sup> or amine/carboxylic acid mixtures.<sup>15,16</sup>

The large-scale development of computers and of high-performance algorithms renders possible the theoretical description of monolayers using different kinds of molecular modeling methods, particularly molecular dynamics simulation of surfactant monolayers.<sup>17,18</sup> However, there are few theoretical papers modeling their behavior during monolayer formation. Therefore, we developed an approach for the

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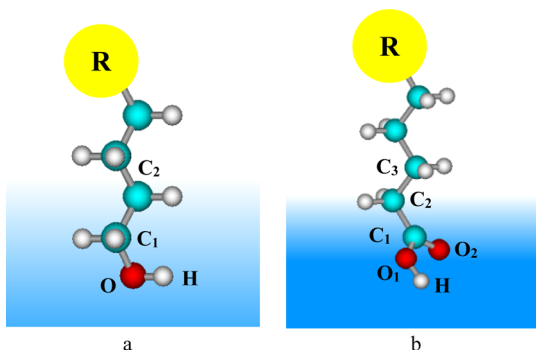
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description of 2D clusterization of nonionic surfactants (aliphatic alcohols,<sup>19,20</sup> carboxylic acids,<sup>21,22</sup> amides,<sup>23</sup>  $\alpha$ -substituted carboxylic acids,<sup>24,25</sup> and so on) at the air/water interface. The values obtained for the calculated alkyl chain length of the surfactants enabling monolayer formation at a given temperature are in agreement with the existing experiments and values of the structural parameters of the corresponding monolayers. This encourages us to now use such an approach for the description of mixed monolayers of nonionic surfactants. The present work aims at the calculation of structural and thermodynamic parameters during the joint clusterization of aliphatic alcohols  $C_nH_{2n+1}OH$  and carboxylic acids  $C_nH_{2n+1}COOH$  ( $n = 6-16$ ) at the air/water interface under standard conditions.

## RESULTS AND DISCUSSION

**Monomers.** We carried out the conformation analysis of alcohol and carboxylic acid monomers in our previous papers.<sup>19-22</sup> Two stable conformers were found for alcohols with the next values of the dihedral angle of the hydroxylic group:  $\angle C2-C1-O-H = 60^\circ$  and  $300^\circ$  ( $-60^\circ$ ) (see Figure 1a). As in ref 19, the values of thermodynamic parameters of



**Figure 1.** Optimized geometric structures of monomers: fatty alcohols (a) and carboxylic acids (b).

the monomer formation were proved to be identical, we use the alcohol conformer with  $\angle\alpha = C2-C1-O-H = 60^\circ$  in the present calculations. The structure of the carboxylic acid monomer is shown in Figure 1b. According to previous investigations,<sup>21,22</sup> the structure with the dihedral angles  $\angle C2-C1-O1-H = 180^\circ$  and  $C3-C2-C1-O2 = -78^\circ$  is energetically most favorable. The surfactant monomers are in the most extended all-trans conformation, as reported by the authors of experimental investigations.<sup>26,27</sup> Such monomer structures are used for the construction of dimers and larger associates of alcohols and carboxylic acids.

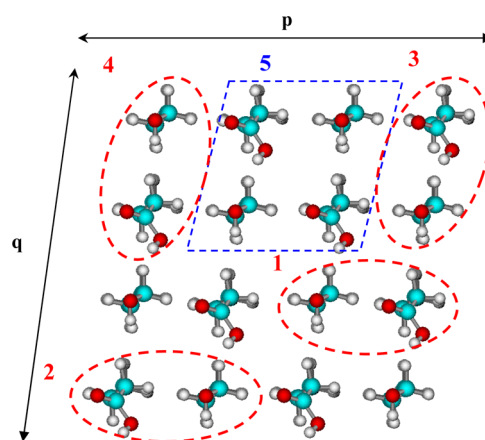
The calculated values of enthalpy, absolute entropy, and Gibbs' energy of monomer formation for alcohols and carboxylic acids agree well with corresponding experimental values.<sup>28</sup> They are listed in our previous papers<sup>21,22</sup> devoted to the investigation of monolayer formation by individual surfactants at the water surface. The calculated values of enthalpy, absolute entropy, and Gibbs' energy of monomer formation are used for the correlation analysis of these values on the alkyl chain length (Table 1). The obtained regressions are linear with corresponding correlation coefficients exceeding 0.9999.

**Small Clusters. Dimers.** In this chapter, mixed dimers of alcohols and carboxylic acids are considered forming after

**Table 1. Correlation Equations of Linear Type:  $y = (a \pm \Delta a)n + (b \pm \Delta b)$  for Alcohol and Carboxylic Acid Monomers (Sampling Amount  $N = 14$ ), where  $n$  Is the Number of Methylene Units in the Alkyl Chain and  $S$  Is the Standard Deviation**

system	parameters	$a \pm \Delta a$	$b \pm \Delta b$	$S$
carboxylic acids <sup>21</sup>	$\Delta H_{298}^0$ , kJ/mol	$-22.68 \pm 0.00$	$-399.47 \pm 0.01$	0.01
	$S_{298}^0$ , J/(mol·K)	$31.57 \pm 0.07$	$267.24 \pm 0.86$	0.79
	$\Delta G_{298}^0$ , kJ/mol	$6.56 \pm 0.02$	$-377.66 \pm 0.17$	0.19
alcohols <sup>29</sup>	$\Delta H_{298}^0$ , kJ/mol	$-22.67 \pm 0.00$	$-199.92 \pm 0.02$	0.03
	$S_{298}^0$ , J/(mol·K)	$33.18 \pm 0.12$	$201.74 \pm 1.23$	1.80
	$\Delta G_{298}^0$ , kJ/mol	$7.95 \pm 0.04$	$-190.59 \pm 0.38$	0.56

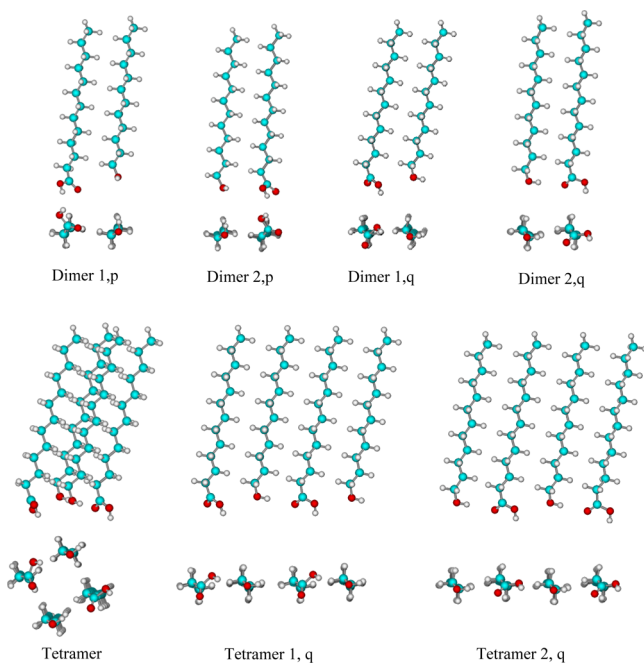
further enlargement of mixed monolayers when molecules of the individual surfactants do not form domains but possess a single distribution of one component into the other. For an extreme case, the fragment of such a monolayer is shown in Figure 2, when alcohols and carboxylic acids are in the ratio of



**Figure 2.** Fragment of geometric structure of infinite 2D cluster 1 of alcohols and carboxylic acids (1:1). Denotation of the basic dimers: 1—dimer 1,  $p$ ; 2—dimer 2,  $p$ ; 3—dimer 1,  $q$ ; 4—dimer 2,  $q$ ; and 5—tetramer.

1:1. Later on, monolayers are regarded, when one of the components is larger. In this case, it is also necessary to consider pure dimers of the individual components. Therefore, one can single out four types of mixed dimers (two in each of  $p$  and  $q$  directions of the spread monolayer) and two types of pure dimers for both components of the mixed monolayer. Four series of mixed dimers with the same number of methylene units in the alkyl chain  $n = 6-16$  are built for further optimization of their geometric structure. It should be noted that it is possible to create mixed films with alcohols and carboxylic acids of different alkyl chain length. Our previous study<sup>29</sup> dealing with penetration of alkanes into alcohol monolayers shows that the calculation of mixed dimer structures with all possible options of alkyl chains for individual components is virtually ineffective concerning the values of the increments for the found  $CH \cdots HC$  interactions using the correlation analysis. Thus, we confine ourselves to considering the series of mixed dimers with the same alkyl chain length.

Optimized geometric structures of the dimers are shown in Figure 3, where associates of alcohols and carboxylic acids



**Figure 3.** Optimized structures of mixed clusters carboxylic acid–alcohol with  $n = 12$  methylene units in the alkyl chain.

possess 10 methylene units in the alkyl chain. For all mentioned dimer structures, we calculated the thermodynamic parameters of their formation and clusterization. Enthalpy, entropy, and Gibbs' energy are calculated according to the following formulas:  $\Delta H_{298,m}^{Cl} = \Delta H_{298}^0 - d \cdot \Delta H_{298,\text{mon(OH)}}^0 - f \cdot \Delta H_{298,\text{mon(COOH)}}^0$ ;  $\Delta S_{298,m}^{Cl} = \Delta S_{298}^0 - d \cdot \Delta S_{298,\text{mon(OH)}}^0 - f \cdot \Delta S_{298,\text{mon(COOH)}}^0$ ; and  $\Delta G_{298,m}^{Cl} = \Delta H_{298,m}^{Cl} - T \cdot \Delta S_{298,m}^{Cl}$  where  $\Delta H_{298}^0$  and  $\Delta S_{298}^0$  are the formation enthalpy and entropy of the corresponding clusters at 298 K;  $H_{298,\text{mon(OH)}}^0$ ,  $S_{298,\text{mon(OH)}}^0$  and  $\Delta H_{298,\text{mon(COOH)}}^0$ ,  $\Delta S_{298,\text{mon(COOH)}}^0$  are the formation enthalpy and entropy of alcohol and carboxylic acid monomers at 298 K, respectively;  $m = d + f$  is the total number of the surfactant molecules in the regarded cluster. The calculated thermodynamic parameters of dimerization of pure and mixed dimers are listed in Table 2.

It should be noted that the structures of the mixed dimers 1,*p* possess edge effects, that is, the value of the dihedral angle C3–C2–C1–O2 differs from the typical value for the most stable monomer conformation. That is why the values of the thermodynamic dimerization parameters for such structures are absent in Table 2. They are also not taken into account when constructing the general correlation dependences of the thermodynamic clusterization parameters on the number of intermolecular CH $\cdots$ HC interactions realized in the regarded cluster. However, we constructed the mixed tetramers of square structure (singled out with the blue dashed line in Figure 2) to assess the increments contributed by the interactions between the functional groups of carboxylic acids and alcohols in dimers 1,*p*. In addition, we constructed two more types of linear tetramers in *q*-direction of the spread monolayer, (see Figure 3), in which the monomers of alcohols and carboxylic acids alternate.

The direct calculation of pure and mixed dimers of alcohols and carboxylic acids shows that alcohol dimerization is possible

for compounds with 10–12 carbon atoms in the alkyl chain, whereas for carboxylic acids, this threshold alkyl chain length is 18–20 carbon atoms. The correlation dependences of the dimerization enthalpy, entropy, and Gibbs' energy on the number of CH $\cdots$ HC interactions are obtained for mixed dimers to assess the contributions of the interactions between the hydrophilic and hydrophobic parts of monomers in the dimers. The regression parameters of the partial correlations are listed in Table 3.

As is obvious from the listed data, the contributions of one CH $\cdots$ HC interaction in the dimerization enthalpy for mixed associates vary within the limits of  $-(10.20\text{--}10.26)$  kJ/mol. Such difference is statistically insignificant within the calculation error. So, this allows uniting the partial correlations into a general one. In addition, the listed values are virtually identical to the corresponding contributions for pure dimers of alcohols and carboxylic acids. For dimerization entropy, one CH $\cdots$ HC interaction contributes  $-(28.10\text{--}29.66)$  J/(mol·K), that is, a somewhat higher modulo than the corresponding values for dimers of the individual compounds. For dimerization Gibbs' energy, the increment of one CH $\cdots$ HC interaction varies within the scope of  $-(1.42\text{--}1.82)$  kJ/mol. The interactions of the hydrophilic parts of surfactants in the mixed dimers contribute insignificantly to the dimerization enthalpy except for dimer 2,*q*, and for pure dimers except for dimer\_OH,*p*. For dimerization entropy and Gibbs' energy, these increments are almost the same for all mixed dimers within the calculation error.

As in our previous works,<sup>20,22</sup> partial correlations for mixed dimers (and square tetramer) are united into a general one

$$\Delta H_{298}^{\text{dim}} = -(10.15 \pm 0.07) \cdot K_a - (2.23 \pm 0.72) \cdot (n_{2,p} + n_{2,q})$$

$$[N = 43; R = 0.9998; S = 2.54 \text{ kJ/mol}] \quad (1)$$

$$\Delta S_{298}^{\text{dim}} = -(23.86 \pm 0.56) \cdot K_a + (32.69 \pm 7.99) \cdot n_{1,p}$$

$$- (100.13 \pm 3.88) \cdot (n_{2,p} + n_{1,q})$$

$$- (109.34 \pm 4.62) \cdot n_{2,q}$$

$$[N = 43; R = 0.9997; S = 11.80 \text{ J/(mol·K)}] \quad (2)$$

$$\Delta G_{298}^{\text{dim}} = -(3.06 \pm 0.12) \cdot K_a - (7.25 \pm 1.72) \cdot n_{1,p}$$

$$+ (28.70 \pm 0.77) \cdot (n_{1,q} + n_{2,q} + n_{2,p})$$

$$[N = 43; R = 0.9881; S = 2.54 \text{ kJ/mol}] \quad (3)$$

where  $K_a$  is a number of intermolecular CH $\cdots$ HC interactions realized in the regarded dimer. It can be found depending on the number of the methylene units in the alkyl chain ( $n_{\text{OH}}$  and  $n_{\text{COOH}}$ ) of the surfactant according to the next formulas:

- for pure dimers of alcohols and carboxylic acids in both directions of the spread monolayer, respectively

$$K_a = \left\{ \frac{n_{\text{OH}}}{2} \right\} \text{ and } K_a = \left\{ \frac{n_{\text{COOH}}}{2} \right\} \quad (4)$$

- for mixed dimers

$$K_a = \min \left[ \left\{ \frac{n_{\text{COOH}} + 1}{2} \right\}; \left\{ \frac{n_{\text{OH}}}{2} \right\} \right] \quad (5)$$

**Table 2. Standard Thermodynamic Parameters of Dimerization/Tetramerization for Pure and Mixed Associates of Alcohols  $C_nH_{2n+1}OH$  and Carboxylic Acids  $C_nH_{2n+1}COOH$  ( $n = 6-16$ ) in PM3 Approximation**

surfactant chain length, $C_nH_{2n+1}$	$\Delta H_{298}^{\text{dim}}$ , kJ/mol	$\Delta S_{298}^{\text{dim}}$ , J/(mol·K)	$\Delta G_{298}^{\text{dim}}$ , kJ/mol	$\Delta H_{298}^{\text{dim}}$ , kJ/mol	$\Delta S_{298}^{\text{dim}}$ , J/(mol·K)	$\Delta G_{298}^{\text{dim}}$ , kJ/mol
	<b>Mixed Tetramer</b>			<b>Mixed Dimer 2,p</b>		
$C_6H_{13}$				-30.93	-154.73	15.18
$C_7H_{15}$	-127.75	-582.44	45.82	-33.51	-165.73	15.88
$C_8H_{17}$	-160.62	-647.42	32.31	-41.27	-182.99	13.26
$C_9H_{19}$	-169.33	-676.00	32.12	-43.86	-193.33	13.75
$C_{10}H_{21}$	-202.31	-741.35	18.61	-51.65	-210.67	11.13
$C_{11}H_{23}$	-211.30	-763.37	16.18	-54.33	-221.23	11.59
$C_{12}H_{25}$	-243.31	-834.60	5.40	-62.05	-242.60	10.25
$C_{13}H_{27}$	-252.88	-861.96	3.98	-64.61	-252.76	10.71
$C_{14}H_{29}$	-285.11	-932.32	-7.28	-72.48	-273.32	8.97
$C_{15}H_{31}$	-294.81	-957.24	-9.55	-75.06	-283.62	9.46
$C_{16}H_{33}$	-326.78	-1020.86	-22.57	-82.80	-299.01	6.30
	<b>Mixed Dimer 1,q</b>			<b>Mixed Dimer 2,q</b>		
$C_6H_{13}$	-29.84	-150.37	14.97	-32.69	-169.14	17.72
$C_7H_{15}$	-32.27	-168.32	17.89	-34.45	-176.48	18.14
$C_8H_{17}$	-40.10	-181.03	13.85	-42.80	-194.89	15.28
$C_9H_{19}$	-42.64	-195.26	15.55	-44.85	-204.16	15.99
$C_{10}H_{21}$	-50.48	-210.93	12.38	-52.85	-215.83	11.47
$C_{11}H_{23}$	-53.13	-222.98	13.31	-55.34	-230.36	13.31
$C_{12}H_{25}$	-60.88	-243.48	11.68	-63.19	-250.70	11.52
$C_{13}H_{27}$	-63.43	-253.68	12.17	-65.63	-261.68	12.35
$C_{14}H_{29}$	-71.31	-275.17	10.69	-73.59	-282.92	10.72
$C_{15}H_{31}$	-73.89	-286.11	11.38	-76.09	-291.16	10.68
$C_{16}H_{33}$	-81.66	-302.96	8.62	-83.89	-309.02	8.20
	<b>Dimer_OH,p</b>			<b>Dimer_OH,q</b>		
$C_6H_{13}$	-31.82	-146.23	11.75	-28.99	-131.46	10.19
$C_7H_{15}$	-34.26	-147.18	9.60	-31.42	-140.96	10.58
$C_8H_{17}$	-42.19	-154.59	3.88	-39.32	-158.11	7.80
$C_9H_{19}$	-44.67	-167.46	5.23	-41.80	-157.16	5.03
$C_{10}H_{21}$	-52.57	-182.90	1.94	-49.69	-159.77	-2.08
$C_{11}H_{23}$	-55.07	-180.43	-1.31	-52.20	-179.82	1.38
$C_{12}H_{25}$	-62.96	-202.51	-2.61	-60.09	-202.45	0.24
$C_{13}H_{27}$	-65.48	-199.67	-5.98	-62.59	-193.18	-5.03
$C_{14}H_{29}$	-73.34	-220.94	-7.50	-70.46	-210.26	-7.80
$C_{15}H_{31}$	-75.88	-222.66	-9.52	-73.00	-218.48	-7.89
$C_{16}H_{33}$	-83.74	-234.57	-13.84	-80.86	-235.49	-10.69
	<b>Dimer_COOH,p</b>			<b>Dimer_COOH,q</b>		
$C_6H_{13}$	-30.19	-161.62	17.97	-30.64	-173.81	21.16
$C_7H_{15}$	-32.89	-183.43	21.78	-33.08	-184.98	22.04
$C_8H_{17}$	-40.38	-188.56	15.81	-40.99	-198.88	18.27
$C_9H_{19}$	-42.94	-200.36	16.76	-43.47	-207.88	18.48
$C_{10}H_{21}$	-50.68	-215.86	13.65	-51.38	-229.00	16.86
$C_{11}H_{23}$	-53.46	-224.26	13.37	-54.10	-232.34	15.14
$C_{12}H_{25}$	-61.04	-242.08	11.10	-61.80	-253.06	13.61
$C_{13}H_{27}$	-63.53	-249.93	10.95	-64.31	-259.79	13.11
$C_{14}H_{29}$	-71.43	-267.15	8.18	-72.27	-279.53	11.03
$C_{15}H_{31}$	-73.99	-273.99	7.66	-74.86	-287.26	10.74
$C_{16}H_{33}$	-81.80	-289.45	4.46	-82.59	-298.95	6.50

The braces denote the integer part of the number.  $n_{1,p}$ ,  $n_{2,p}$ ,  $n_{1,q}$ , and  $n_{2,q}$  are the identifiers of the interactions between the functional groups of alcohol and carboxylic acid in the dimer structures. If, for example,  $n_{1,p} = 1$ , then such interaction realizes in the regarded dimer, otherwise it does not.

Consider in detail, how the number of  $CH\cdots HC$  interactions depends on the surfactant alkyl chain length in the case that they are different. For example, if the alkyl chain length for alcohol  $n_{OH} = 10$  and for carboxylic acid  $n_{COOH} = 6$  methylene units, then such a dimer has three  $CH\cdots HC$  interactions. For

longer carboxylic acids with  $n_{COOH} = 7$  or 8 and the same alcohol decanol, the number of  $CH\cdots HC$  interactions is one more (namely, four) than in the previous case. For carboxylic acids with even longer alkyl chains by 1–2 methylene fragments and the same decanol, the number of  $CH\cdots HC$  interactions in the dimer reaches the maximum (with five). Further lengthening of the carboxylic acid alkyl chain does not affect the number of  $CH\cdots HC$  interactions in case of the chosen alcohol. Therefore, the highest possible number of such interactions is defined by the length of the shorter surfactant in



**Table 3. Parameters of Partial Correlations for Pure and Mixed Associates of Alcohols and Carboxylic Acids:  $y = (a \pm \Delta a) \bullet K_a + (b \pm \Delta b)$  ( $K_a$  Is a Number of Intermolecular CH $\cdots$ HC-Interactions Realized in the Regarded Cluster; Sampling Amount  $N = 11$ )**

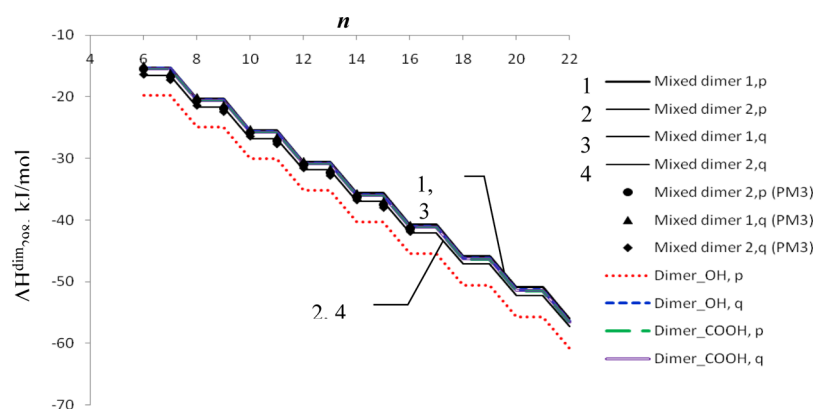
System	$(a \pm \Delta a)$	$(b \pm \Delta b)$	R	S
		$\Delta H_{298}^{\text{Cl}}$ , kJ/mol		
dimer_OH, <i>p</i>	$-10.29 \pm 0.26$	$-8.61 \pm 1.28$	0.997	1.36
dimer_OH, <i>q</i>	$-10.26 \pm 0.26$		0.997	1.35
dimer_COOH, <i>p</i>	$-10.30 \pm 0.33$		0.996	1.47
dimer_COOH, <i>q</i>	$-10.29 \pm 0.26$		0.997	1.39
mixed dimer 2, <i>p</i>	$-10.26 \pm 0.27$		0.997	1.41
mixed dimer 1, <i>q</i>	$-10.26 \pm 0.27$		0.997	1.39
mixed dimer 2, <i>q</i>	$-10.20 \pm 0.23$	$-3.28 \pm 1.28$	0.998	1.42
square tetramer_OH	$-10.27 \pm 0.21$		0.998	4.50
linear tetramer_OH	$-10.32 \pm 0.23$	$-6.55 \pm 3.79$	0.998	3.65
square tetramer_COOH	$-10.43 \pm 0.29$		0.997	5.24
linear tetramer_COOH	$-10.35 \pm 0.29$		0.997	3.84
mixed square tetramer	$-10.32 \pm 0.25$		0.997	5.29
mixed linear tetramer 1, <i>q</i>	$-10.26 \pm 0.22$		0.998	3.58
mixed linear tetramer 2, <i>q</i>	$-10.24 \pm 0.22$	$-6.07 \pm 3.63$	0.998	3.49
		$\Delta S_{298}^{\text{Cl}}$ , J/(mol·K)		
dimer_OH, <i>p</i>	$-23.93 \pm 1.74$	$-96.21 \pm 8.68$	0.993	3.87
dimer_OH, <i>q</i>	$-19.78 \pm 1.27$	$-76.33 \pm 7.00$	0.982	6.75
dimer_COOH, <i>p</i>	$-24.76 \pm 1.59$	$-96.28 \pm 11.70$	0.984	7.13
dimer_COOH, <i>q</i>	$-25.14 \pm 0.95$	$-104.32 \pm 5.26$	0.994	5.07
mixed dimer 2, <i>p</i>	$-28.84 \pm 1.14$	$-73.41 \pm 6.29$	0.993	6.06
mixed dimer 1, <i>q</i>	$-29.66 \pm 1.39$	$-70.02 \pm 7.65$	0.990	7.37
mixed dimer 2, <i>q</i>	$-28.10 \pm 1.16$	$-86.95 \pm 6.41$	0.992	6.18
square tetramer_OH	$-16.04 \pm 0.85$	$-322.16 \pm 18.68$	0.988	18.00
linear tetramer_OH	$-25.08 \pm 1.24$	$-266.81 \pm 18.96$	0.992	16.16
square tetramer_COOH	$-21.98 \pm 0.99$	$-341.88 \pm 20.65$	0.992	17.74
linear tetramer_COOH	$-29.05 \pm 1.87$	$-251.61 \pm 29.22$	0.984	25.15
mixed square tetramer	$-21.77 \pm 0.78$	$-313.44 \pm 17.16$	0.994	16.53
mixed linear tetramer 1, <i>q</i>	$-27.73 \pm 1.11$	$-251.34 \pm 16.55$	0.994	13.17
mixed linear tetramer 2, <i>q</i>	$-27.25 \pm 1.61$	$-268.70 \pm 22.38$	0.990	15.26
		$\Delta G_{298}^{\text{Cl}}$ , kJ/mol		
dimer_OH, <i>p</i>	$-3.16 \pm 0.39$	$20.06 \pm 1.96$	0.985	1.43
dimer_OH, <i>q</i>	$-4.37 \pm 0.36$	$23.19 \pm 1.99$	0.971	1.92
dimer_COOH, <i>p</i>	$-2.97 \pm 0.19$	$28.52 \pm 1.02$	0.983	0.98
dimer_COOH, <i>q</i>	$-2.80 \pm 0.13$	$29.94 \pm 0.70$	0.991	0.67
mixed dimer 2, <i>p</i>	$-1.66 \pm 0.10$	$20.28 \pm 0.57$	0.983	0.55
mixed dimer 1, <i>q</i>	$-1.42 \pm 0.18$	$20.46 \pm 0.97$	0.937	0.94
mixed dimer 2, <i>q</i>	$-1.82 \pm 0.17$	$22.83 \pm 0.94$	0.963	0.90
square tetramer_OH	$-5.49 \pm 0.28$	$92.50 \pm 6.22$	0.988	5.99
linear tetramer_OH	$-3.01 \pm 0.16$	$74.92 \pm 2.45$	0.990	2.09
square tetramer_COOH	$-3.88 \pm 0.07$	$102.76 \pm 1.52$	0.999	1.31
linear tetramer_COOH	$-2.81 \pm 0.22$	$87.79 \pm 3.03$	0.982	2.07
mixed square tetramer	$-3.83 \pm 0.04$	$88.47 \pm 0.82$	0.999	4.79
mixed linear tetramer 1, <i>q</i>	$-1.93 \pm 0.13$	$70.90 \pm 1.97$	0.984	1.57
mixed linear tetramer 2, <i>q</i>	$-2.20 \pm 0.13$	$75.00 \pm 1.87$	0.989	1.28

the considered pair. Before the maximum is reached, the number of CH $\cdots$ HC interactions depends stepwise on the alkyl chain length of the surfactant with the shorter hydrophobic part.

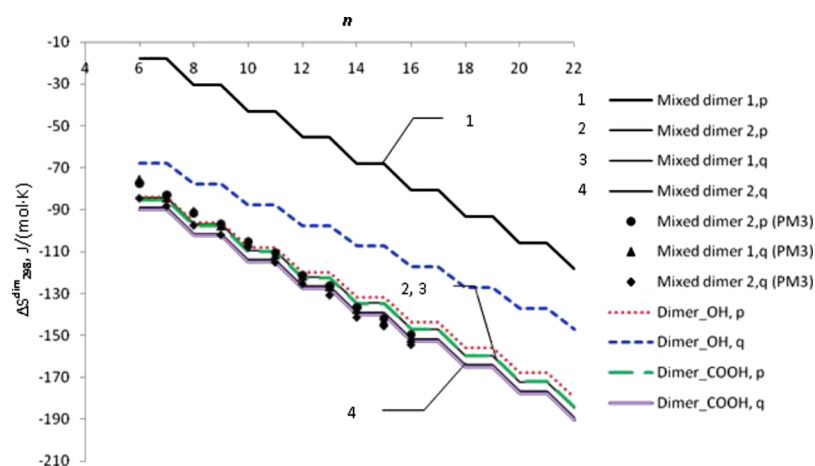
Figures 4–6 show the graphs of the dependences of the dimerization parameters for mixed and pure dimers on the alkyl chain length (in the case where  $n_{\text{OH}} = n_{\text{COOH}}$ ). Here, the black solid lines define the dependences calculated according to the correlation eqs 1–3; the dots stand for the results of the direct calculations with the PM3 method. The dependences for the pure dimers calculated in the previous studies<sup>20,22</sup> are also shown in Figures 4–6 for comparison. It is clear that the data

of the direct calculations are in good agreement with predicted values. As can be seen, dimer 1,*p* is energetically most advantageous among the four types of mixed dimers. The formation of such mixed dimers is also more preferable than pure alcohol or carboxylic acid dimers. The formation of mixed dimers of other types is less preferable. However, the formation of mixed dimers is slightly more advantageous than the formation of pure carboxylic acid dimers.

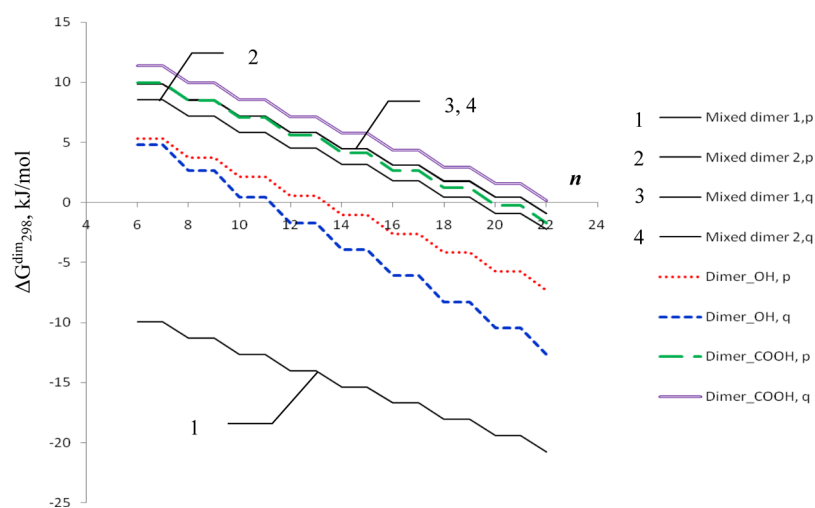
**Tetramers.** Figure 7 shows the graphs of the tetramerization Gibbs' energy for mixed tetramers of the linear and square structures (see Figure 3) to illustrate the energetic effect of alcohol–carboxylic acid interaction in comparison to for-



**Figure 4.** Dependence of variation of dimerization enthalpy for pure and mixed dimers on the number of methylene units in the surfactant alkyl chain.



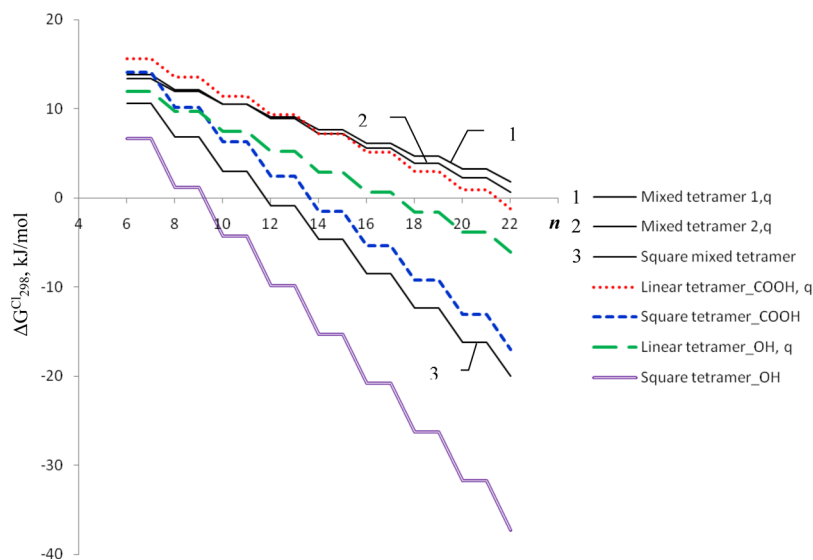
**Figure 5.** Dependence of variation of dimerization entropy for pure and mixed dimers on the number of methylene units in the surfactant alkyl chain.



**Figure 6.** Dependence of variation of dimerization Gibbs' energy for pure and mixed dimers on the number of methylene units in the surfactant alkyl chain.

mation of pure clusters. Partial correlations for tetramers of pure alcohols and carboxylic acids were obtained in our previous studies.<sup>20–22,29</sup> The corresponding parameters for the dependences of tetramerization enthalpy, entropy, and Gibbs' energy on the number of  $\text{CH}\cdots\text{HC}$  interactions in the associates are listed in Table 3.

As can be seen in Figure 7, the formation of mixed linear tetramers is almost isoenergetic with the formation of mixed linear tetramers of carboxylic acids and essentially less preferable in comparison to the formation of alcohol ones. The formation of square mixed tetramers is possible for compounds with  $n = 12$  methylene units in the alkyl chain.



**Figure 7.** Dependence of variation of the clusterization Gibbs' energy for pure and mixed tetramers on the number of methylene units in the surfactant alkyl chain.

This is an average value between alcohol and carboxylic acid threshold alkyl chain length enabling aggregation to tetramers (10 and 14 methylene units, respectively). Thus, it is possible to assume that interactions realized between monomers in *p*-direction of the spread monolayer are more preferable within the clusterization Gibbs' energy than ones realized in the other direction. It may be caused by the hydrogen interactions between hydrogen of the acid carboxylic group and oxygen of the alcohol hydroxylic group realized in the associates in *q*-direction. Our previous calculations<sup>21</sup> have shown that the presence of hydrogen bonds during the interaction of the surfactant polar parts leads to a more positive contribution to the clusterization Gibbs' energy.

The contributions of the polar head group interactions and CH $\cdots$ HC interactions are singled out after the unification of the partial correlations for dimers and tetramers. These contributions will be used below for defining the thermodynamic clusterization parameters for large and infinite 2D clusters using the additive scheme. It should be noted that the increment of the CH $\cdots$ HC interactions obtained for mixed and pure associates of alcohols and carboxylic acids are almost the same:  $-10.27$ ,  $-10.39$ ,  $-10.10$  kJ/mol for clusterization enthalpy and  $-25.12$ ,  $-19.72$ ,  $-23.07$  J/(mol·K) for clusterization entropy, respectively. In addition, the structure is the same for mixed small clusters and pure ones from the point of view of the number and type of CH $\cdots$ HC interactions. Therefore, we united the partial correlation dependences for mixed and pure clusters into a general one to construct the additive scheme enabling calculation of the parameters for the joint clusterization of fatty alcohols and carboxylic acids. The final general correlation is in the next form

$$\begin{aligned} \Delta H_{298}^{\text{Cl}} = & -(10.35 \pm 0.03) \cdot K_a + (4.04 \pm 1.13) \cdot n_{1,p} \\ & - (1.44 \pm 0.32) \cdot (n_{2,p} - n_{\text{OH},q}) \\ & - (2.14 \pm 0.49) \cdot n_{2,q} \end{aligned} \quad (6)$$

[ $N = 140$ ;  $R = 0.9998$ ;  $S = 3.10$  kJ/mol]

$$\begin{aligned} \Delta S_{298}^{\text{Cl}} = & -(21.99 \pm 0.64) \cdot K_a + (19.98 \pm 11.29) \cdot n_{1,p} \\ & - (112.66 \pm 3.46) \cdot (n_{2,p} + n_{1,q} + n_{2,q} \\ & + n_{\text{COOH},p}) - (18.47 \pm 5.67) \cdot n_{\text{OH},p} \\ & - (93.05 \pm 4.26) \cdot n_{\text{OH},p} - (58.16 \pm 5.82) \cdot \\ & n_{\text{COOH},q} \end{aligned} \quad (7)$$

[ $N = 140$ ;  $R = 0.9986$ ;  $S = 28.10$  J/(mol·K)]

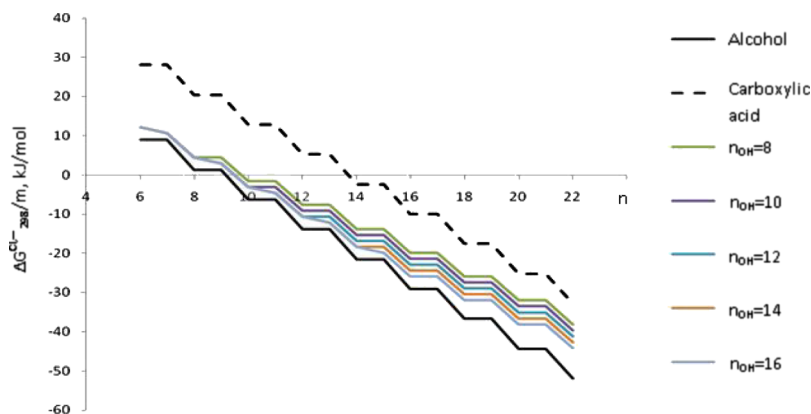
$$\begin{aligned} \Delta G_{298}^{\text{Cl}} = & -(3.81 \pm 0.17) \cdot K_a - (4.03 \pm 2.89) \cdot n_{1,p} \\ & + (32.53 \pm 0.88) \cdot (n_{1,q} + n_{2,p} + n_{2,q} + n_{\text{COOH},q}) \\ & + (5.27 \pm 1.45) \cdot n_{\text{OH},p} + (25.82 \pm 1.09) \cdot n_{\text{OH},p} \\ & + (17.36 \pm 1.48) \cdot n_{\text{COOH},q} \end{aligned} \quad (8)$$

[ $N = 140$ ;  $R = 0.9705$ ;  $S = 7.19$  kJ/mol]

where  $n_{1,p}$ ,  $n_{2,p}$ ,  $n_{1,q}$  and  $n_{2,q}$  are the identifiers of interactions between the functional head groups in the mixed associate as in the corresponding mixed dimer structures;  $n_{\text{OH},p}$ ,  $n_{\text{OH},q}$ ,  $n_{\text{COOH},q}$  and  $n_{\text{COOH},q}$  are the identifiers of interactions between the functional head groups in the pure associates of alcohols and carboxylic acids, respectively. If interactions between the functional groups of the monomer head groups exist in the cluster, the value of the corresponding identifier is equal to the number of such interactions, otherwise this identifier is zero.  $K_a$  is the number of CH $\cdots$ HC interactions realized in the regarded cluster.

**Large and Infinite Clusters.** This chapter deals with two types of monolayers: 2D film 1 with single distribution of the first surfactant molecules among molecules of the second one and 2D film 2 of domain structure, when amphiphilic molecules associate into homogeneous domains of the same molecules with their later linkage.

**2D Film 1 with Single Distribution of the First Surfactant in the Second One.** Several structural fragments can be singled out between carboxylic acid and alcohol molecules in 2D film 1 that contribute to values of the



**Figure 8.** Dependence of variation of clusterization Gibbs' energy per surfactant molecule of mixed 2D films 1 on the number of the methylene units in the surfactant alkyl chain ( $n$ ) at  $X_{\text{COOH}} = 10\%$  mol.

clusterization thermodynamic parameters. They are  $\text{CH}\cdots\text{HC}$  interactions and four types of interactions between the hydrophilic parts of carboxylic acid and alcohol. According to Figure 2, these interactions are identical in dimer  $1,p$  and  $2,p$  in  $p$  direction of the spread monolayer and identical in dimer  $1,q$  and  $2,q$  in  $q$  direction. The interactions between the polar head groups of the same surfactant type should also be taken into account. The number of mixed interactions in  $p$  and  $q$  directions is defined as  $n_{1,p}$ ,  $n_{2,p}$  and  $n_{1,q}$ ,  $n_{2,q}$ . The number of interactions between the same surfactant molecules is defined as  $n_{\text{OH},p}$ ,  $n_{\text{OH},q}$  for alcohols and  $n_{\text{COOH},p}$  and  $n_{\text{COOH},q}$  for carboxylic acids. It is easy to determine the number of all interactions described above independently of the orientation of the alcohol and carboxylic acid molecules in the monolayer (provided the molecules of the component with smaller molar fraction are not situated side by side but surrounded by molecules of the component with bigger molar fraction) as

$$\begin{aligned} n_{1,p} &= n_{2,p} = n_{1,q} = n_{2,q} = 0.5X \cdot pq \\ n_{\text{OH}/\text{COOH},p} &= q(p-1) - 2X \cdot pq \\ n_{\text{OH}/\text{COOH},q} &= p(q-1) - 2X \cdot pq \end{aligned} \quad (9)$$

where  $X$  is the molar fraction of the minor component in the associate or film;  $p$  and  $q$  are the numbers of molecules that construct the cluster in the corresponding directions.

The dependence of the number of  $\text{CH}\cdots\text{HC}$  interactions on the alkyl chain length is defined as

$$\begin{aligned} K_a &= [(q(p-1) - 2X \cdot pq) + (p(q-1) - 2X \cdot pq)] \cdot \\ &\left\{ \frac{n_{\text{OH}/\text{COOH}}}{2} \right\} + 4X \cdot pq \cdot \min \left[ \left\{ \frac{n_{\text{COOH}} + 1}{2} \right\} \right. \\ &\left. ; \left\{ \frac{n_{\text{OH}}}{2} \right\} \right] \end{aligned} \quad (10)$$

where  $n_{\text{COOH}}$  and  $n_{\text{OH}}$  are the numbers of methylene units in the hydrocarbon chain of carboxylic acids and alcohols, respectively; the braces denote the integer part of the number.

To obtain the parameters per one monomer molecule of 2D film, one should use the procedure that became standard for such series of studies. Expressions 6–8 should be divided by the total number of monomers in the cluster ( $m = p \cdot q$ ). After that, one has to calculate the limits of the resulting expressions at infinite number of molecules in the cluster. Then, expressions 6–8 assume the next form for the 2D film 1 ( $p$

$= \infty$ ,  $q = \infty$ ) possessing all types of interactions between the functional groups of the surfactants described above

$$\begin{aligned} n_{1,p}^{\infty}/m &= n_{2,p}^{\infty}/m = n_{1,q}^{\infty}/m = n_{2,q}^{\infty}/m = 0.5X, \\ n_{\text{OH}/\text{COOH},p}^{\infty}/m &= n_{\text{OH}/\text{COOH},q}^{\infty}/m = 1 - 2X \end{aligned} \quad (11)$$

The number of  $\text{CH}\cdots\text{HC}$  interactions per one molecule of the monolayer can be calculated according to the formula

$$\begin{aligned} K_a^{\infty}/m &= 2 \cdot ((1 - 2X) \cdot \left\{ \frac{n_{\text{COOH}/\text{OH}}}{2} \right\} \\ &+ 2X \cdot \min \left[ \left\{ \frac{n_{\text{COOH}} + 1}{2} \right\}; \left\{ \frac{n_{\text{OH}}}{2} \right\} \right]) \end{aligned} \quad (12)$$

After substitution of eqs 11 and 12 in the correlation equations for calculation of clusterization enthalpy, entropy, and Gibbs' energy, 6–8, one obtains expressions for calculation of these parameters per one surfactant molecule of the monolayer depending on the surfactant alkyl chain length and molar fraction. In the case that  $X_{\text{COOH}} < 0.5$ , such expressions possess the forms

$$\Delta H_{298}^{\text{Cl},\infty}/m = -10.36 \cdot K_a^{\infty}/m + 3.34 \cdot X_{\text{COOH}} - 1.44 \quad (13)$$

$$\Delta S_{298}^{\text{Cl},\infty}/m = -21.99 \cdot K_a^{\infty}/m - 94.95 \cdot X_{\text{COOH}} - 111.52 \quad (14)$$

$$\Delta G_{298}^{\text{Cl},\infty}/m = -3.81 \cdot K_a^{\infty}/m + 31.64 \cdot X_{\text{COOH}} + 31.79 \quad (15)$$

If the molar fraction of carboxylic acids exceeds 0.5, the expressions for clusterization enthalpy, entropy, and Gibbs' energy per monomer molecule are

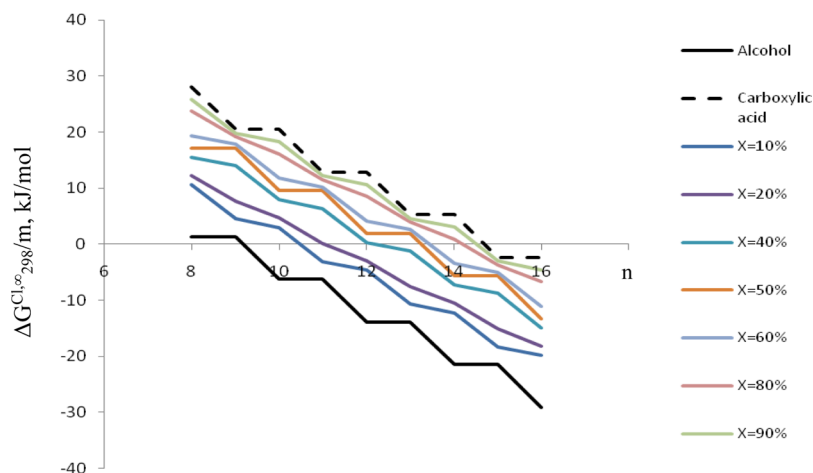
$$\Delta H_{298}^{\text{Cl},\infty}/m = -10.36 \cdot K_a^{\infty}/m + 0.46 \cdot X_{\text{OH}} \quad (16)$$

$$\Delta S_{298}^{\text{Cl},\infty}/m = -21.99 \cdot K_a^{\infty}/m + 23.65 \cdot X_{\text{OH}} - 111.52 \quad (17)$$

$$\Delta G_{298}^{\text{Cl},\infty}/m = -3.81 \cdot K_a^{\infty}/m - 6.59 \cdot X_{\text{OH}} + 50.90 \quad (18)$$

Here,  $K_a^{\infty}/m$  is the number of intermolecular  $\text{CH}\cdots\text{HC}$  interactions per surfactant molecule in the mixed 2D film 1 (see eq 12). As follows from the listed expressions, the contribution of the carboxylic acid–alcohol interactions to the clusterization Gibbs' energy is almost identical to the pure





**Figure 9.** Dependence of variation of clusterization Gibbs' energy per surfactant molecule of mixed 2D films 1 on the carboxylic acid molar fraction  $X$  ( $n$  is the number of carbon atoms in the surfactant alkyl chain).

alcohol interactions and essentially more preferable than pure carboxylic acid ones.

The dependences of  $\Delta G_{298}^{Cl,\infty}/m$  on the number of methylene fragments in the surfactant alkyl chain are shown in Figure 8 when the monolayer contains  $X = 10\%$  mol of carboxylic acids. Here, the black solid line corresponds to the formation of the pure alcohol monolayer and the black dashed line to the formation of pure carboxylic acid monolayer. The colored lines represent the formation of mixed alcohol–carboxylic acid monolayers with the given alcohol alkyl chain length and carboxylic acids with  $n_{\text{COOH}} = 6\text{--}22$  methylene units in the alkyl chain. As is evident from Figure 8, the shorter the carboxylic acid alkyl chain introduced into the alcohol monolayer, the less preferable is the formation of such a film in comparison to more long-chained alcohol. This is corroborated by the fact that the number of  $\text{CH}\cdots\text{HC}$  interactions is smaller in case of inequality of alcohol and carboxylic acid alkyl chain lengths in comparison to the maximum possible number for the compound with longer alkyl chain. In addition, the energetic contribution of carboxylic acid–alcohol interactions is slightly larger than that for pure alcohols. Note that the increase of the carboxylic acid molar fraction in the alcohol monolayer does not change the character of the described dependences, but the colored lines are more extended along the ordinate axis.

It is interesting to estimate the effect of the increase of molar fraction for one of the components on the preference of the mixed film formation in the case that alcohols and carboxylic acids have the same alkyl chain length. As is evident from Figure 9, the  $\Delta G_{298}^{Cl,\infty}/m$  dependences for mixed films are limited by the corresponding dependences for pure components from both sides. Therefore, it is possible to suppose that there are no synergetic interactions between the two hydrophilic parts of the different surfactants. The formation of mixed films is more favorable than pure carboxylic acid clusterization but less favorable than the formation of pure alcohol films. This is in agreement with the existing experimental data concerning the study of surface pressure–molecular area ( $\pi$ – $A$ ) isotherms of pure and mixed monolayers of tetradecanol and tetradecanoic acid.<sup>14</sup> The formation of monolayers with equimolar content of the components is most preferable among other possible component proportions. This is called forth by the fact that

such monolayers possess the same number of  $\text{CH}\cdots\text{HC}$  interactions as monolayers of pure alcohols, whereas the number of these interactions decreases with the increase of carboxylic acid molar fraction in the mixture.

#### 2D Films 2 with Domain Distribution of Surfactants.

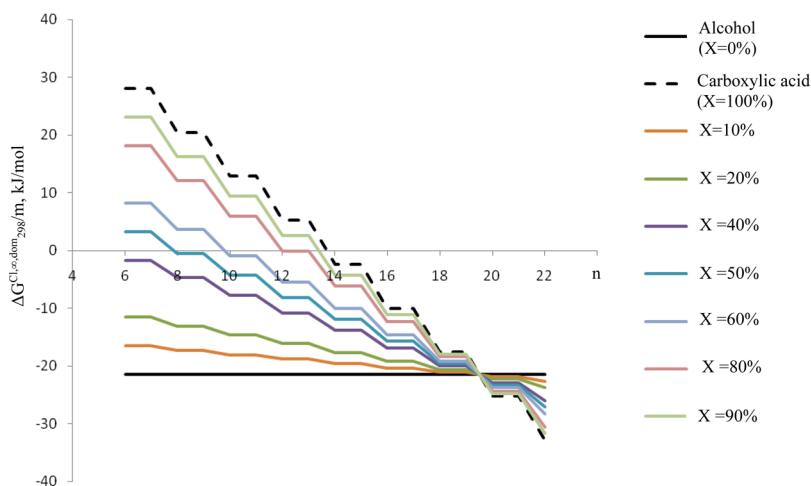
In such films, the amphiphilic molecules of the same class form clusters surrounded by the clusters of the other component. Here, the interactions between the hydrophilic parts of different surfactants should be taken into account, as in our previous study devoted to alkane clusterization in the presence of alcohols.<sup>30</sup> However, the number of such interactions in limit tends to zero when obtaining the clusterization parameters per one molecule of the monolayer. That is why the thermodynamic clusterization parameters of such films,  $A_{298}^{Cl,\infty,\text{dom}}/m$ , can be calculated as weighted average sum of the corresponding parameters for monolayer formation of pure components: alcohol  $A_{298}^{Cl,\infty,\text{OH}}/m$  and carboxylic acid  $A_{298}^{Cl,\infty,\text{COOH}}/m$ . That means,  $A_{298}^{Cl,\infty,\text{dom}}/m = X \cdot A_{298}^{Cl,\infty,\text{COOH}}/m + (1 - X) \cdot A_{298}^{Cl,\infty,\text{OH}}/m$ , where  $X$  is the molar fraction of the carboxylic acid in the mixed monolayer. The contributions of the interactions realized between the alcohol hydrophilic parts are  $-1.44$  kJ/mol for clusterization enthalpy,  $-111.52$  J/(mol·K) for entropy, and  $31.79$  kJ/mol for Gibbs' energy. For carboxylic acids, these contributions are  $-170.82$  J/(mol·K) and  $50.90$  kJ/mol for entropy and Gibbs' energy, respectively, whereas for clusterization enthalpy, the increment of the head group interaction is statistically insignificant. Then, the expressions for calculation of the thermodynamic clusterization parameters per surfactant molecule of the mixed 2D films 2 are as follows

$$\Delta H_{298}^{Cl,\infty,\text{dom}}/m = -10.36 \cdot K_a^\infty/m + 1.44 \cdot X - 1.44 \quad (19)$$

$$\Delta S_{298}^{Cl,\infty,\text{dom}}/m = -21.99 \cdot K_a^\infty/m - 59.3 \cdot X - 111.52 \quad (20)$$

$$\Delta G_{298}^{Cl,\infty,\text{dom}}/m = -3.81 \cdot K_a^\infty/m + 19.11 \cdot X + 31.79 \quad (21)$$

where,  $X$  is the molar fraction of carboxylic acids in the monolayer;  $K_a^\infty/m$  is the number of intermolecular  $\text{CH}\cdots\text{HC}$  interactions per surfactant molecule in the 2D film and depends on the number of methylene units in the surfactant alkyl chain ( $n$ ) as  $2 \cdot \{n/2\}$ .



**Figure 10.** Dependence of  $\Delta G_{298}^{Cl,\infty,dom}/m$  on the carboxylic acid content in the films ( $X$ , % mol) at given alcohol alkyl chain length (tetradecanol is taken as an example;  $n$  is the number of methylene units in the surfactant alkyl chain).

The graphical dependences of clusterization Gibbs' energy per surfactant molecule of mixed films with domain structure are shown in Figure 10. Here, the black solid line corresponds to  $\Delta G_{298}^{Cl,\infty}/m$  for pure tetradecanol, and the black dashed line corresponds to  $\Delta G_{298}^{Cl,\infty}/m$  for carboxylic acids with  $n = 6$ –16 methylene units in the alkyl chain. The group of colored lines corresponds to the dependences of  $\Delta G_{298}^{Cl,\infty,dom}/m$  for mixed films with the domain structure obtained on the basis of tetradecanol and carboxylic acid homologues with different content in the monolayer.

It is interesting to discover how the alkyl chain length of carboxylic acids and alcohols affects the preferable formation of the considered types of mixed films. The thermodynamic condition of preferable formation of a mixed monolayer with single distribution of one component among another in comparison to a monolayer with the domain structure is the following inequality

$$\Delta \Delta G_{298}^{Cl,\infty}/m = [\Delta G_{298}^{Cl,\infty}/m - \Delta G_{298}^{Cl,\infty,dom}/m] \leq 0 \quad (22)$$

It is necessary to take into account that  $\Delta G_{298}^{Cl,\infty}/m$  for 2D film 1 can be generally expressed as

$$\Delta G_{298}^{Cl,\infty}/m = U \cdot K_a^\infty/m + (1 - 2X) \cdot V^{OH} + 2X \cdot A \text{ at } X < 0.5 \quad (23)$$

$$\Delta G_{298}^{Cl,\infty}/m = U \cdot K_a^\infty/m + (1 - 2X) \cdot V^{COOH} + 2(1 - X) \cdot A \text{ at } X > 0.5 \quad (24)$$

where,  $X$  is molar fraction of carboxylic acids in the alcohol monolayer;  $K_a^\infty/m$  is the number of intermolecular  $CH \cdots HC$  interactions per surfactant molecule in the 2D film;  $U$  is the contribution of one  $CH \cdots HC$  interaction to the clusterization Gibbs' energy ( $-3.81$  kJ/mol);  $V^{OH}$  and  $V^{COOH}$  are the contributions of hydrophilic head group interactions for individual surfactants:  $31.79$  and  $50.90$  kJ/mol for alcohols and carboxylic acids, respectively; and  $A$  is the contribution of hydrophilic head group interactions in the mixed pairs "alcohol–carboxylic acid" ( $47.61$  kJ/mol).

For 2D films 2 with domain structure

$$\Delta G_{298}^{Cl,\infty,dom}/m = U \cdot K_a^\infty/m + V^{OH} - X \cdot (V^{OH} - V^{COOH}) \text{ at } X < 0.5 \quad (25)$$

$$\Delta G_{298}^{Cl,\infty,dom}/m = U \cdot K_a^\infty/m + V^{COOH} - X \cdot (V^{COOH} - V^{OH}) \text{ at } X > 0.5 \quad (26)$$

When subtracting eqs 25, 26 from 23 and 24, respectively, it is possible to obtain the expression for  $\Delta \Delta G_{298}^{Cl,\infty}/m$ . This expression is valid for any value of  $X$  (from 0 to 1)

$$\Delta \Delta G_{298}^{Cl,\infty}/m = [U_i \cdot \Delta K_a^\infty/m - X \cdot (V^{OH} + V^{COOH}) + 2 \cdot A \cdot X] \leq 0 \quad (27)$$

where,  $X$  is molar fraction of carboxylic acids in the alcohol monolayer; and  $\Delta K_a^\infty/m$  is the number of intermolecular  $CH \cdots HC$  interactions per surfactant molecule in film lost because of the difference in the alkyl chain lengths of alcohols and carboxylic acids.

As it follows from eq 12, the value of  $\Delta K_a^\infty/m$  depends on the alkyl chain length of the corresponding surfactants and the molar fraction of the components in the monolayer. The value  $\Delta K_a^\infty/m$  can be calculated as

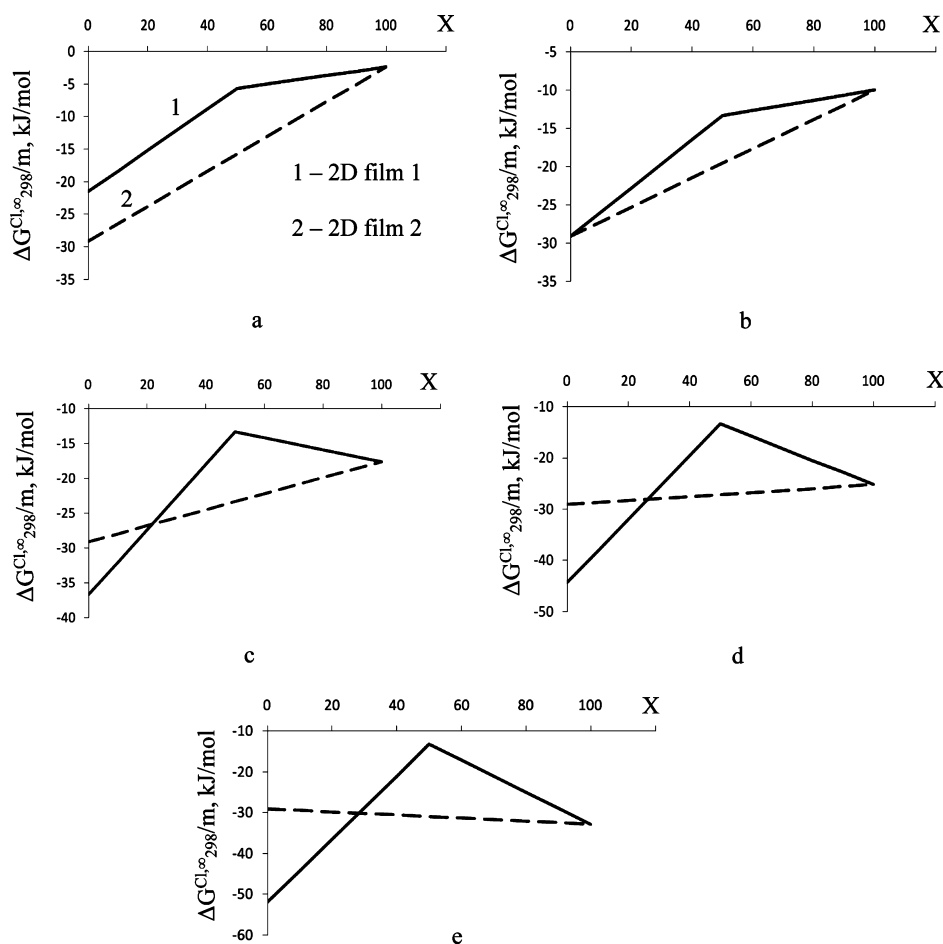
$$\Delta K_a^\infty/m = 4X \cdot \left( \min \left[ \left\{ \frac{n_{COOH} + 1}{2} \right\}; \left\{ \frac{n_{OH}}{2} \right\} \right] - \left\{ \frac{n_{OH}}{2} \right\} \right) \quad (28)$$

where,  $n_{COOH}$  and  $n_{OH}$  are the numbers of the methylene units in the hydrocarbon chain of carboxylic acids and alcohols, respectively; the braces denote the integer part of the number.

Finally, the inequality 27 transforms into the following

$$\left\{ \frac{n_{COOH} + 1}{2} \right\} - \left\{ \frac{n_{OH}}{2} \right\} \leq \frac{V^{OH} + V^{COOH} - 2A}{4U} \quad (29)$$

The value of  $\left\{ \frac{n_{COOH} + 1}{2} \right\} - \left\{ \frac{n_{OH}}{2} \right\}$  is equal to 0 or 1 (for even and odd values of  $n$ ) if both surfactants possess the same number of  $CH_2$ -units in the alkyl chain. After substitution of the contributions for all interactions and on account of the previous fact, it is found that  $\left\{ \frac{n_{COOH} + 1}{2} \right\} - \left\{ \frac{n_{OH}}{2} \right\}$  should exceed 1 or 2. This means that the formation of mixed films with single distribution of surfactant among the molecules of the other component is advantageous if the carboxylic acid alkyl chain length is longer than that of the corresponding alcohol by 1–2 methylene units. For example, the structure of the 2D film 1 is more favorable than that of the 2D film 2 for octanol or nonanol ( $n_{OH} = 8$  or  $9$ ) and carboxylic acids from undecanoic acid ( $n_{COOH} = 10$  methylene units in the alkyl chain except for the carbon atom of the carboxylic group). In



**Figure 11.** Dependence,  $\Delta G_{298}^{Cl,\infty}/m$ , on the carboxylic acid content in films ( $X$ , % mol.) at given alkyl chain length of alcohol (hexadecanol taken as an example) and carboxylic acid: (a)  $n_{COOH} = 14$ , (b)  $n_{COOH} = 16$ , (c)  $n_{COOH} = 18$ , (d)  $n_{COOH} = 20$ , and (e)  $n_{COOH} = 22$ .

case of decanol and undecanol, the corresponding carboxylic acids should have more than 12 methylene units in the alkyl chain.

It is also necessary to determine the content of surfactant mixtures when the 2D film 1 is more preferred provided the condition described above is fulfilled. The clusterization Gibbs' energy per surfactant monomer for 2D film 1 can be expressed in the following way

$$\Delta G_{298}^{Cl,\infty}/m = \Delta G_{298}^{Cl,\infty,OH}/m + U \cdot \Delta n - 2U \cdot X \cdot \Delta n + A' \cdot X \quad (30)$$

where,  $\Delta G_{298}^{Cl,\infty,OH}/m$  is the clusterization Gibbs' energy for alcohol with the given alkyl chain length.

$\Delta n$  is the difference of the surfactant alkyl chain lengths;  $X$  is molar fraction of carboxylic acids in the alcohol monolayer;  $A'$  corresponds to the value of the  $X$  held constant in eq 21; and  $U$  has the same meaning as in eqs 23–26.

The clusterization Gibbs' energy per surfactant monomer of the 2D film 2 can be written down in the following form

$$\Delta G_{298}^{Cl,\infty,dom}/m = \Delta G_{298}^{Cl,\infty,OH}/m + U \cdot X \cdot \Delta n + X \cdot (V^{COOH} - V^{OH}) \quad (31)$$

where,  $\Delta G_{298}^{Cl,\infty,OH}/m$  is the clusterization Gibbs' energy for alcohol with the given alkyl chain length;  $\Delta n$  is the difference of the surfactant alkyl chain lengths;  $X$  is the molar fraction of carboxylic acids in the alcohol monolayer; and  $U$ ,  $V^{OH}$ , and  $V^{COOH}$  have the same meaning as in eqs 23–26.

Using the condition (eq 22) mentioned above, it is possible to obtain the expression for  $X$  when the formation of 2D film 1 is more advantageous than 2D film 2

$$X \leq \frac{U \cdot \Delta n}{3U \cdot \Delta n - A' + V^{COOH} - V^{OH}} \quad (32)$$

The obtained fractionally linear dependence can be illustrated using hexadecanol ( $n_{OH} = 16$ ) and carboxylic acids with  $n_{COOH} = 8$ –22 methylene units in the alkyl chain taken as an example. As is evident from Figure 11, the elongation of the carboxylic acid alkyl chain in comparison to the chosen alcohol leads to a change of the monolayer structure. For example, hexadecanol and carboxylic acids with  $n_{COOH} = 8$ –16 methylene fragments in the alkyl chain form mixed films with domain structure at any component proportion (see Figure 11a,b).

However, if the carboxylic acid length reaches  $n_{COOH} = 18$  methylene units, the alkyl chain length difference  $\Delta n = 2$ . According to the condition (eq 29) described above, this leads to more preferable formation of 2D films 1 with single distribution of carboxylic acid molecules in the alcohol monolayer. Such preference is preserved for the carboxylic acid content  $X \leq 21.5\%$  mol (see Figure 11c). In case that carboxylic acid has even longer hydrophobic chain in comparison to the chosen alcohol, the preferable carboxylic acid content increases to  $X \leq 26.2$  and 28.2% mol for carboxylic acids with  $n_{COOH} = 20$  and 22.5, respectively (see

Figure 11d,e). As follows from eq 32, the maximum content of carboxylic acid is  $X = 33.3\%$  mol for the limiting case, when the difference in carboxylic acid and alcohol alkyl chain lengths tends to infinity.

The obtained data agree with the results of the experimental studies for mixed monolayers of tetradecanoic, pentadecanoic, and octadecanoic acids with tetradecanol and hexadecanol. The authors of ref 14 give the dependences of equilibrium pressure for the LE-LC phase transition on the carboxylic acid content. These dependences are linear and possess a kink point that can be associated with the possible change of the monolayer structure.

## CONCLUSIONS

This study introduces a theoretical analysis of the joint film formation of aliphatic alcohols  $C_nH_{2n+1}OH$  and carboxylic acids  $C_nH_{2n+1}COOH$  ( $n = 6-16$ ) at the air/water interface in the framework of the quantum-chemical semiempirical PM3 method. The calculation of the thermodynamic parameters of formation and clusterization of small mixed aggregates shows that destabilizing contributions of interactions of the surfactant hydrophilic parts to clusterization Gibbs' energy are essentially smaller than the corresponding contributions for pure carboxylic acids and exceeds the contributions for pure alcohols. This allows the assumption that the absence of synergy between the regarded surfactants is lacking while the formation of mixed monolayers.

Two types of mixed films are considered: 2D film 1 with single distribution of the first component in the second and 2D film 2 with the domain structure. The conditions for the competitive formation of these films are dependent on the surfactant alkyl chain lengths and their content in the mixture. The calculations show that the preferable formation of 2D film 1 is possible, provided (1) the carboxylic acid alkyl chain is longer than that of the corresponding alcohol by 1–2 methylene units and (2) the carboxylic acid content should not exceed the value  $X \leq \frac{3.81 \cdot \Delta n}{3 \times 3.81 \cdot \Delta n + 12.53}$  (in the limit  $33.3\%$  mol at  $\Delta n \rightarrow \infty$ ).

The proposed approach can be the basis for theoretical studies of other binary mixtures of nonionic surfactants at the air/water interface. It enables us to predict the structure of possible mixed monolayers depending on the surfactant alkyl chain length and molar fraction in the mixture.

## METHOD AND MODEL OF CALCULATIONS

The calculation of the thermodynamic parameters of the joint clusterization of aliphatic alcohols and carboxylic acids at the air/water interface is done using the quantum-chemical program package Mopac 2000<sup>31</sup> in the framework of semiempirical PM3 method. This method is parameterized within the formation heats<sup>32,33</sup> and describes adequately the experimental data concerning the monolayer formation by different nonionic surfactant classes<sup>19–22</sup> despite some restrictions.<sup>34</sup>

The calculation of the thermodynamic clusterization parameters of aliphatic alcohols and carboxylic acids is carried out using the quantum-chemical model described in details elsewhere.<sup>35</sup> Here, we provide only its key points:

- intermolecular  $CH \cdots HC$  interactions between the methylene units of the hydrocarbon chains of the interacting surfactant molecules contribute mainly to the value of the clusterization Gibbs' energy;

- intermolecular  $CH \cdots HC$  interactions are additive in pairs;
- influence of the interface is taken into account implicitly via its orientating and stretching effect on the surfactant molecule, when it is in the all-trans conformation;
- thermodynamic clusterization parameters of the regarded surfactants are calculated using supermolecular approximation;
- the additive scheme is constructed using data obtained for small clusters (dimers, trimers, and tetramers). It represents the values of the thermodynamic clusterization parameters as total contributions of the  $CH \cdots HC$  interactions realized in the cluster and the interactions between the hydrophilic parts of the surfactants. This scheme takes into account only the  $CH \cdots HC$  interactions realized between the methylene units of the nearest surfactant molecules as the energy of the intermolecular interaction declines rapidly proportionally to  $r^{-6}$ ;
- on the basis of the described additive scheme, the thermodynamic parameters of film formation are calculated using the limiting values.

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### Notes

The authors declare no competing financial interest.

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