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Relationship between the Bulk and Surface Basicity of Aliphatic Amines: A Quantum Chemical Approach

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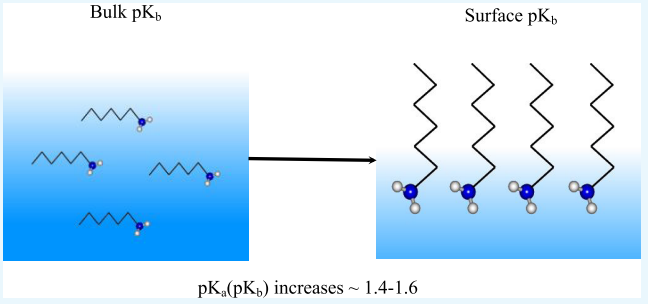
ABSTRACT: To assess the surface basicity constant (pK_b) of aliphatic amine films, the use of a theoretical approach recently developed to evaluate the pK_a of carboxylic acid monolayers on the water surface is tested. The present paper gives a new full picture of the change of acid−base properties of surfactants during their aggregation at the air/water interface. The exploited approach is simple because it does not involve the construction of thermodynamic cycles but uses the Gibbs energies of the formation and dimerization of surfactant monomers in neutral and ionized forms in the aqueous and gaseous phases. The quantum chemical semiempirical PM3 method is applied to perform calculations using a conductor-like screening model, which takes into account the aqueous phase. The calculation shows that aliphatic amines, as well as carboxylic acids, are characterized by a change of the value of the basicity/acidity constant during the film formation. The film formation of surfactants leads to a decrease in their acid−base properties, i.e., the surface pK_a values of carboxylic acids and pK_b values of amines increase. However, unlike carboxylic acids, there is practically no dependence of the surface pK_b value on the alkyl chain length of the aliphatic amine, which is caused by almost identical contributions of one CH_2 fragment to the solvation Gibbs energy of neutral and ionized monomers within the calculation error. The obtained results agree with existing experimental data.



INTRODUCTION

It is known that many factors affect the structure and stability of mono- and multimolecular surfactant films. The most significant of them include the surface activity of the amphiphile, the structure of the hydrocarbon chain, as well as the interaction between the polar groups of amphiphilic molecules in a monolayer.[1−3] In the latter case, the nature of this interaction is affected by the presence of specific electrolytes in the aqueous phase, as well as the solution pH.[4−6] In addition, an important value is the dissociation/protonation constant, which determines the ability of a substance to release/attach protons, mostly expressed as pK_a/pK_b. Note that, in the literature from the given pair of constants, the pK_a value is mostly used even for substances that exhibit basic properties. However, taking into account the simple relationship between these constants ($pK_b = 14 - pK_a$), it is easy to find one knowing the other. Despite the fact that there are fairly accurate experimental methods for determining pK_a, in some cases, this is a difficult task when the test substances are, for example, very weak or, conversely, very strong acids. Therefore, along with the experimental methods, calculation methods are also widely used for estimation.[7−9] In modern studies,[10−12] it was found that a significant part of the organic functional group composition of atmospheric marine aerosol particles falls on hydroxyl, alkane, amine, and carboxylic acid functional groups. This stipulates interest to investigate the acid−base properties of surfactants with such head groups during their aggregation at air/water interface that can affect the properties of the surface microlayer and further aerosol particles formed from it.

It should also be noted that most of the studies are focused on the estimation of the pK_a (pK_b) values for surfactants in the bulk phase, whereas there is much less information about the surface layer of such compounds. Most thoroughly examined in this field is the class of saturated and unsaturated carboxylic acids,[13,14] whereas for aliphatic amine monolayers, such studies are much rare, and surface pK_a values available in the literature relate to the early works of Glazer,[15] Porter,[16] and Betts[17] that differ from each other. It should be noted that in the past 3 decades, the interface selective nonlinear optical process of the second harmonic generation (SHG) method has been widely used to estimate the pK_a value of surfactant monolayers.[5] However, unlike carboxylic acids, for aliphatic amines, data are available only for a few representatives of the homologous

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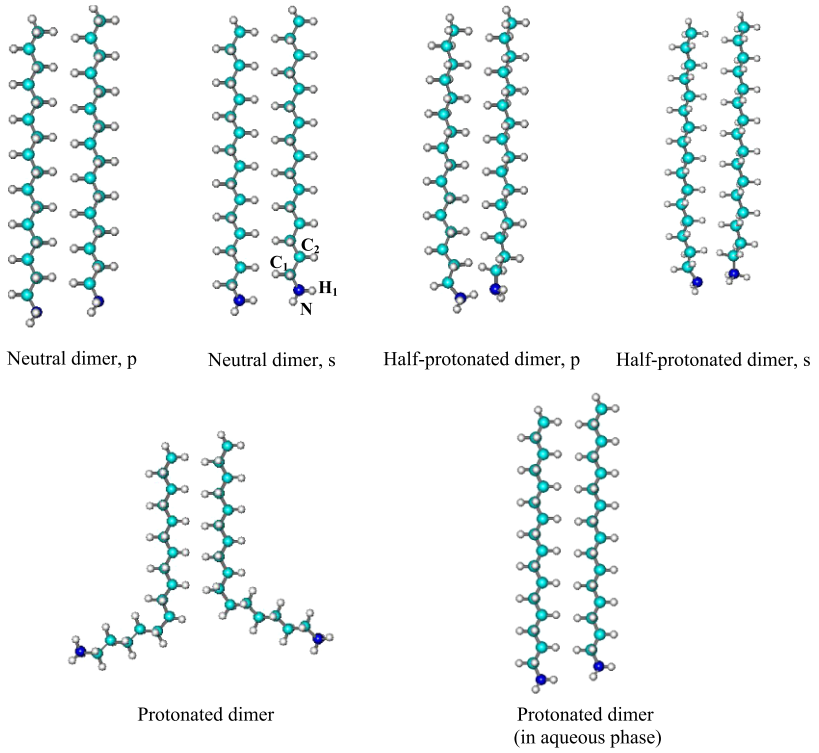

Figure 1. Optimized geometric structures of amine dimers in the gaseous phase.

series with an alkyl chain length of 17−19 and 22 carbon atoms.[15,16,18,19] These data show that the pK_a value of aliphatic amines changes at aggregation, as well as in the case of carboxylic acids, but with the only difference that the pK_a value shifts, on the contrary, toward more neutral pH values. Since in our recent work we developed an adequate scheme for estimation of the surface exponent of the dissociation constant[20] for carboxylic acids during monolayer formation, it gives an impetus to testing it for assessment of the protonation constant exponent by the example of aliphatic amines. Moreover, it is not absolutely obvious that if the scheme works on acids, then it will work on bases. The compounds with basic properties will extend the statistical material to check the adequacy of the theory proposed for acidic compounds. Considering all of the above, the objective of this work is to estimate the protonation constants of aliphatic amines $C_nH_{2n+1}NH_2$ (n = 6−16) during monolayer formation at the air/water interface in the framework of the quantum chemical approach.

RESULTS AND DISCUSSION

Monomers. As in our earlier study,[21] now, we consider the structures of aliphatic amines in which the hydrocarbon chain is in the most elongated "linear" conformation. According to the conformational analysis, three stable conformations of the monomers are determined with the following values of the amino group torsion angle $\angle C_2{-}C_1{-}N{-}H_1$ = 60, 180, and 300° (Figure 1). The conformational analysis of amine dimers carried out in the same paper showed that the most stable dimer structures are those based on the first conformer. Here, we also consider precisely this structure of amine monomers. The thermodynamic parameters for the formation of amine monomers in neutral and ionized forms with chain lengths from 1 to 16 carbon atoms were calculated in the gaseous and water phases. The correlation dependences of the enthalpy, entropy, and Gibbs' energy of monomer formation on the chain length were constructed (Table 1). The corresponding correlation coefficients varied within the limits of 0.95−0.99. Note that according to the data of Gibbs energy the formation of amine monomers is more preferable in the gaseous phase compared with that in the aqueous phase both for the neutral and charged forms of amines. This is also characteristic of the case of carboxylic acids considered in our recent work.[17]

Table 1. Correlation Equations for the Thermodynamic Formation Parameters on the Alkyl Chain Length of the Form: $y = (a \pm \Delta a)\cdot n + (b \pm \Delta b)$ for Amine Monomers[a]

characteristics	$a \pm \Delta a$	$b \pm \Delta b$	S
Neutral Form in the Gaseous Phase			
ΔH_{298}^0, kJ/mol	−22.67 ± 0.00	−199.92 ± 0.02	0.03
S_{298}^0, J/(mol·K)	33.18 ± 0.12	201.74 ± 1.23	1.80
ΔG_{298}^0, kJ/mol	7.95 ± 0.04	−190.59 ± 0.38	0.56
Protonated Form in the Gaseous Phase			
ΔH_{298}^0, kJ/mol	−23.15 ± 0.21	651.76 ± 2.09	3.98
S_{298}^0, J/(mol·K)	32.31 ± 0.04	223.98 ± 0.49	0.87
ΔG_{298}^0, kJ/mol	7.82 ± 0.22	695.69 ± 2.16	4.12
Neutral Form in the Water Phase			
ΔH_{298}^0, kJ/mol	−21.59 ± 0.43	−21.21 ± 4.20	8.02
S_{298}^0, J/(mol·K)	29.45 ± 0.43	217.38 ± 4.17	7.96
ΔG_{298}^0, kJ/mol	10.23 ± 0.44	2.14 ± 4.34	8.29
Protonated Form in the Water Phase			
ΔH_{298}^0, kJ/mol	−22.37 ± 0.05	618.34 ± 0.51	0.64
S_{298}^0, J/(mol·K)	28.71 ± 0.57	245.29 ± 6.09	7.69
ΔG_{298}^0, kJ/mol	9.68 ± 0.19	652.82 ± 2.03	2.56

[a]Sample size N = 16, n is the number of methylene units in the chain, and S is the standard deviation.

In numerous works,[22−24] a linear correlation of the protonation/deprotonation Gibbs energy of compounds in

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water with experimental data is used to estimate the pK_a value. Based on the available calculated data for the formation Gibbs energy of the cation ΔG_{cat}^{water} and the neutral monomer ΔG_{neu}^{water} in water, it is also possible to obtain the dependence of pK_b for monomers on the difference of these energies $\Delta G_{cat}^{water} - \Delta G_{neu}^{water}$. The available experimental data for the series from methyl to octyl amine is used. The obtained dependence has the following form

$$pK_b^{bulk} = 0.434\frac{\Delta G_{cat}^{water} - \Delta G_{neu}^{water}}{RT} + 2.38 \quad (1)$$

The bulk pK_b data of amines calculated by eq 1 are given in Table 2.

Table 2. Bulk and Surface pK_b Values for the Homologous Series of Amines

	bulk pK_b (monomers)		surface pK_b (monolayer)	
compound	calcd in PM3 according to eq 1	exptl[25−27]	calcd according to eq 4	exptl
CH_3NH_2	3.32	3.36		
$C_2H_5NH_2$	3.32	3.25		
$C_3H_7NH_2$	3.33	3.47		
$C_4H_9NH_2$	3.43	3.40		
$C_5H_{11}NH_2$	3.43	3.40		
$C_6H_{13}NH_2$	3.43	3.40	5.01	
$C_7H_{15}NH_2$	3.43	3.40	4.97	
$C_8H_{17}NH_2$	3.43	3.43	4.97	
$C_9H_{19}NH_2$	3.43		4.95	
$C_{10}H_{21}NH_2$	3.42		4.97	
$C_{11}H_{23}NH_2$	3.43		4.97	
$C_{12}H_{25}NH_2$	3.42		5.00	
$C_{13}H_{27}NH_2$	3.42		4.96	
$C_{14}H_{29}NH_2$	3.42		5.00	
$C_{15}H_{31}NH_2$	3.43		4.95	
$C_{16}H_{33}NH_2$	3.43		5.06	
$C_{17}H_{35}NH_2$	3.43		4.90	
$C_{18}H_{37}NH_2$	3.43		4.88	5.5[15]
				4.5[19]
$C_{19}H_{39}NH_2$	3.43		4.87	4.1[17]
$C_{20}H_{41}NH_2$	3.43		4.85	
$C_{21}H_{43}NH_2$	3.43		4.84	
$C_{22}H_{45}NH_2$	3.43		4.82	4.1[18]
				3.9[5]

Dimers. In this section, we consider two types of basic dimers, which take part in the further construction of a two-dimensional (2D) film. These are dimers with the so-called "parallel" and "sequential" arrangement of functional groups in them. In Figure 2, their names are marked with the letters "p" and "s", respectively. Such differentiation is conditional and based on the mutual arrangement of vectors in the dimer, which are drawn through the centers of hydrogen atoms of amino groups in the hydrophilic parts of surfactants. For neutral and half-protonated dimers shown in Figure 1, their thermodynamic parameters of formation and dimerization in the gaseous and aqueous phases are calculated. These parameters correlate with the number of intermolecular CH···HC interactions. The corresponding coefficients in linear expressions are listed in Table 3. The correlation analysis shows that the contributions of the intermolecular CH···HC interactions to the dimerization Gibbs energy differ by almost ten times for systems in vacuum and water. The contributions

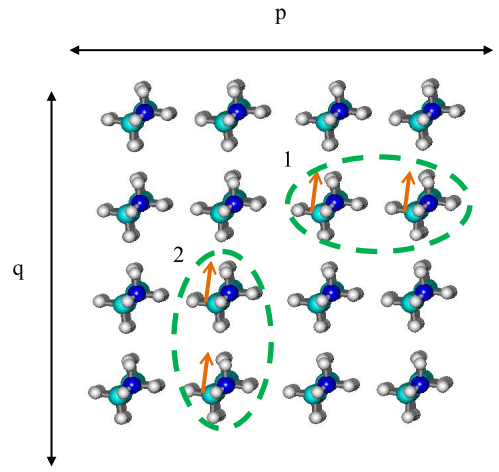

Figure 2. Fragment of a neutral 2D film of amines (bottom view) with the designation of the basic dimers: (1) parallel dimer, p, and (2) sequential dimer, s.

Table 3. Parameters of Partial Correlations for Dimerization Gibbs' Energy of Amines (ΔG_{298}^{dim}, kJ/mol): $y = (a \pm \Delta a)\cdot K_a + (b \pm \Delta b)$[a]

system	$(a \pm \Delta a)$	$(b \pm \Delta b)$	R	S
neutral dimer, p	−2.40 ± 0.13	20.81 ± 0.72	0.987	0.70
neutral dimer, s	−2.38 ± 0.12	22.19 ± 0.69	0.988	0.66
half-protonated dimer, p	−2.92 ± 0.10	−13.15 ± 0.58	0.994	0.56
half-protonated dimer, s	−2.81 ± 0.19	−4.94 ± 1.06	0.979	1.03
neutral dimer, p (COSMO)	−23.31 ± 1.57	140.15 ± 6.51	0.993	3.85
neutral dimer, s (COSMO)	−23.08 ± 2.67	129.23 ± 0.987	0.987	6.54
half-protonated dimer, p (COSMO)	−19.62 ± 0.06	110.86 ± 20.95	0.999	0.10
half-protonated dimer, s (COSMO)	−25.16 ± 3.87	134.43 ± 16.89	0.966	10.10

[a] K_a is the number of intermolecular CH···HC interactions realized in the regarded dimer and calculated as an integer part of $n/2$; n is the number of carbon atoms in the amine alkyl chain; sampling amount N = 11 or 6 for COSMO.

of the interactions of the neutral functional groups of amines in water are 6−7 times higher than those for similar systems in vacuum. For half-protonated amine dimers, these contributions are significantly more favorable in the gaseous phase than in the aqueous phase and more preferable than the contributions of the neutral amino group interactions.

Figure 3 shows the graphic dependences of ΔG_{298}^{dim} for associates calculated in both phases using the example of parallel dimer structures. The lines designate the values calculated from the correlation dependences, and the points show the results of the direct calculation in the PM3 method. Although the results of calculations with taking into account the solvent in the COSMO model have a larger standard deviation, it can be seen that the dimerization of amines in the neutral form and in the form of a half-protonated associate in the aqueous phase is characteristic of compounds with a chain length of 14−16 carbon atoms. Shorter-chain amines are stable under vacuum in the form of a half-protonated dimer. The obtained results generally reflect the available experimental

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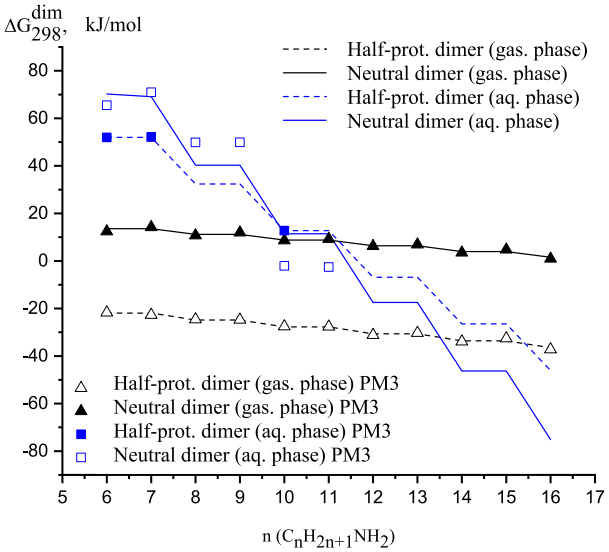

Figure 3. Dependence of the dimerization Gibbs energy on the amine chain length.

data. In the study in ref 28, π-A isotherms are obtained for $C_{17}H_{35}NH_2$ in water with pH ~ 6 and 10^{-3} M NaOH. On the water surface with pH ~ 6, amine molecules are in a partially protonated state, and the resulting monolayer is characterized by a slightly smaller area per one molecule. At more acidic pH values, amine molecules are completely ionized, which leads to the formation of more stretched monolayers with lower surface viscosity than similar monolayers at the alkaline subphase (pH = 9.0−9.5).[17,29]

2D Films. In a previous paper,[30] we developed a "simple method", which allowed assessing the clusterization thermodynamic parameters per monomer of a 2D film using corresponding dimerization parameters only for structures with a certain arrangement of the dipole moments of the head groups. This makes it possible to estimate the value of the thermodynamic parameters of film clusterization using only the contributions of the headgroup interactions for dimers and not to calculate large clusters to construct an additive scheme. For this, the thermodynamic parameters of dimerization should be added. Another study[31] has proven that the nature of intermolecular CH···HC interactions realized between the hydrophobic chains is the same for 11 examined surfactant classes. Therefore, here we use the values of these contributions to the clusterization Gibbs energy estimated in ref 30. Then, the expressions for clusterization Gibbs energy per one amine molecule in the film are as follows

$$\Delta G^{Cl}_{neu}/m = -5,6\cdot\left\{\frac{n}{2}\right\} + 44.51 \text{ for neutral monolayer} \quad (2)$$

$$\Delta G^{Cl}_{an}/m = -5,6\cdot\left\{\frac{n}{2}\right\} - 18.09 \text{ for half} - \text{protonated monolayer} \quad (3)$$

where n is the number of methylene fragments in the amine chain and braces {...} denote the integer part of the number.

Then, using formula 4 from the Theory section and substituting $\Delta G^{Cl}_{298}/m$ expressions (2) and (3) into it, the pK_b values for amine monolayers with different alkyl chain lengths can be calculated. A comparison of the contributions of clusterization and solvation Gibbs energies of the neutral and protonated forms of amine molecules shows the following situation. The surfactant chain lengthening does not affect the value of the contribution from the difference in clusterization Gibbs energies of the neutral and half-ionized monolayers. This contribution is 62.6 kJ/mol. The same picture is typical also for carboxylic acid monolayers. For them, this value is four times lower and amounts to 15.45 kJ/mol. As for the contributions of one methylene fragment to the solvation Gibbs energy of the neutral amine monomer and cation, they are almost identical, and their difference is only 0.07 kJ/mol, unlike carboxylic acids. This leads to the fact that the surface pK_b of the amine monolayer differs from the bulk pK_b but is practically independent of the surfactant alkyl chain length. The average contribution of one methylene fragment to the change in the surface pK_b value is 0.01 units, which is statistically insignificant, taking into account the estimation error of the applied scheme.

As already noted in our recent work,[20] the PM3 method overestimates the energy of intermolecular CH···HC interactions.[32] This leads to an overestimation of the clusterization Gibbs energies per monomer of surfactant films twice as much as the values obtained from the analysis of experimental data according to the theoretical model of Fainerman et al.[21,33] This model uses parameters such as critical point coordinates, area per molecule in the condensed state, and aggregation number for small aggregates in the liquid-expanded monolayer to calculate the formation Gibbs energy of a surfactant 2D cluster using experimentally obtained π-A isotherms. Excluding this fact, the surface pK_b values estimated from eq 4 have a standard deviation from Glazer's experimental data[15] of 5.05. Taking this fact into account by reducing twice the values of $\Delta G^{Cl}_{neu}/m$ and $\Delta G^{Cl}_{cat}/m$ from eqs 2 and 3 in the calculation of the surface pK_b improved significantly the agreement between the calculated and experimental data with the standard deviation from Glazer's experimental data[15] of 0.56 units and 0.44 from the Binks' data.[19] We performed the same procedure recently for the calculation of pK_a of carboxylic acids, which also has led to good agreement between the calculated data and the more numerous experiments in the literature with a standard deviation of 0.22 units. This speaks in favor of the adequacy of the correction used by us, which is associated with the peculiarities of the PM3 parameterization. The results of surface pK_b calculations with correction are given in Table 2 and reflect qualitatively the scarcely available experimental data. They show that the pK_b value of amine films differs from that for monomers in the bulk phase to a greater extent but does not depend on their alkyl chain length. Available experimental and theoretical studies[15−17,34] show that the shift of the pK_a (pK_b) values for amines is in the range of 0.7−1.0 units. Testing the proposed approach on the two classes of surfactants—carboxylic acids and amines—has shown that it adequately reproduces the pK_a and pK_b of monolayers at the air/water interface and they can be used for prognostic purposes.

CONCLUSIONS

An approach for assessment of the value of the surface index of the basicity constant for aliphatic amines at the air/water interface is tested, previously proposed for calculation of the surface pK_a for carboxylic acids. The approach is based on the pairwise additivity of intermolecular CH···HC interactions between interacting amphiphilic compounds. This makes it

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Table 4. Energy and Length of CH···HC Bonds Estimated Using Different Methods

method	energy of CH···HC bond, kJ/mol	length of CH···HC bond, Å	reference
CCSD(T)	2.22;		38
	6.31		39
ωB97XD/6-311++G(d,p)	0.84−2.82	2.3−2.6	40
B3LYP6-31G**//B3LYP6-31G**	3.3−16.7		41, 42
MP2 with BSSE and 6−311++G(3df,3pd)	0.52−1.6	2.50−3.03 Å	43
MP2 and MP4 with 6−311++G(3df,3pd)	0.52	2.5	44
DFT-D/cc-PVTZ		1.78−1.91	45
PM3	2.81−4.93	1.7−1.8	our calculations
PM6	9.20	1.7	our calculations
PM7	4.18	1.5	our calculations

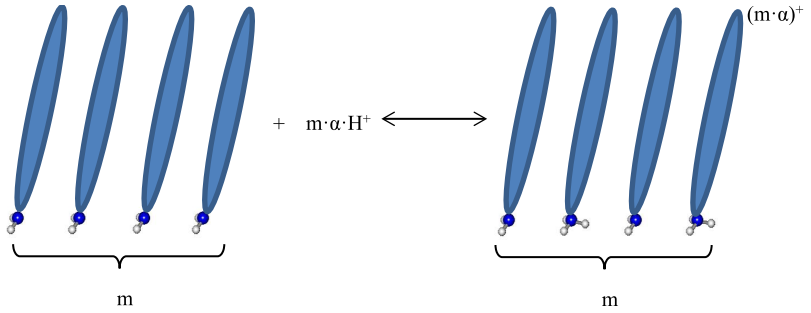

Figure 4. Scheme of the amine cluster protonation with α = 0.5 (m = 4 for this case).

possible to calculate the Gibbs energies of the formation of neutral and half-protonated surfactant films using the corresponding parameters of monomers and dimers in the aqueous and gaseous phases. Using these data, it is easy to calculate the surface pK_b of the monolayer. The calculations show that for aliphatic amines, as well as for carboxylic acids, the surface pK_b (pK_a) value differs from that of the bulk phase. Moreover, the basicity of amines in the monolayer decreases compared to the same value for monomers, as well as the acidity of carboxylic acids decreases when they are aggregated. However, for aliphatic amines, the dependence of the surface pK_b on the alkyl chain length is practically not observable since the contributions of one methylene fragment to the solvation Gibbs energy of neutral and ionized monomers almost coincide.

The described approach allows us to identify the relationship between the bulk and surface pK_a (pK_b) values, as well as to use both theoretical and experimental values. The proposed scheme gives a quantum chemical interpretation of the available experimental data and can be used for prognostic purposes.

CALCULATION METHOD

To calculate thermodynamic and structural parameters of aliphatic amine monomers and dimers, we use the Mopac2000 software package[35] with the quantum chemical semiempirical PM3 method[36] and applied successfully[21,37] to calculate enthalpy, entropy, and Gibbs energy of clusterization of amines and ten other surfactant classes on the water surface. It allows the adequate evaluation of a number of parameters, such as the threshold surfactant chain length at which solid-crystalline monolayers are formed, the geometric unit cell parameters of the condensed monolayers, the "temperature effect" of clusterization, morphological features of surfactant monolayer formation at a given temperature, and chain length. Now, PM3 has been upgraded to PM6 and PM7. However, after comparison of different methods, we make sure that the results concerning energy and length of CH···HC bonds obtained with PM3 are better, while calculating time is reasonable comparing to ab initio methods (see Table 4 below). In addition, this method showed the adequate capability to calculate the pK_a value for carboxylic acid monolayers.[17] Therefore, the PM3 method is used in the present work. The calculation of the thermodynamic parameters of surfactant monomers and dimers in water is carried out as part of the conductor-like screening model (COSMO).[46] It should be noted that in a later version of Mopac2016,[47] it is possible to calculate directly the pK_a values of substances using the PM6 method in the COSMO model, but such a possibility is realized only for compounds with the −O−H bond, i.e., unlike carboxylic acids, it is not feasible for amines.

THEORY

Our recent paper proposes an approach to calculate the surface pK_a of amphiphilic films using the clusterization Gibbs energy of neutral and ionized molecules for carboxylic acids.[20] Since the thermodynamic parameters of the formation and clusterization of surfactants are pairwise additive, the clusterization Gibbs energy of large and infinite associates can be assessed on the basis of the dimerization Gibbs energy of surfactants in two directions of the spread monolayer. To do so, it is sufficient to calculate the dimerization Gibbs energies of three types of dimers: a neutral (nonionized) dimer, a half-ionized dimer, and a completely ionized dimer. Based on these data, it is possible to calculate the clusterization Gibbs energy of an aliphatic amine monolayer with the desired degree of protonation α as the weighted average sum of the corresponding dimerization parameters of various types of dimers. Figure 1 shows the geometrical structures of these dimers optimized in the gas phase except for the last structure, which is optimized in the aqueous phase. Clusterization

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thermodynamic parameters of the surfactant calculated exactly in the gas phase are used in further pK_b calculations. Two possible mutual arrangements of amine monomers in dimers with the so-called sequential and parallel arrangement of the functional groups in two possible directions of the monolayer propagation are also considered.[21] In Figure 1, the corresponding structures are marked with the letters s and p, respectively. Hydrogen bonding of one of the hydrogen atoms of the NH_3^+ group and nitrogen of the neutral amine molecule is present in the half-protonated amine dimers. After optimization of the last completely ionized dimer, the obtained structure in the gaseous phase differs significantly from those of the other two types of dimers in Figure 4. It possesses strong mutual repulsion of two positively charged ammonia groups. However, optimization of such a cationic dimer in the COSMO approximation gets the structure similar to other dimers in a neutral and half-protonated form, i.e., strong repulsion of NH_3^+ groups is not observed. However, the positive value of dimerization Gibbs energy for such dimer does not speak in favor of its formation.

We have obtained dependences of the clusterization Gibbs energy per one monomer of an associate, consisting of the three described types of dimers using hexadecylamine as an example. This dependence $\Delta G^{Cl}/m$ is obtained from dimerization Gibbs energies per monomer for different dimer types taken in a weighted average ratio depending on the degree of protonation. It has the form of a V-shaped broken line with a minimum corresponding to the degree of protonation $\alpha = 0.5$ both for the calculated data obtained in the gaseous phase and with account for the aqueous phase in the COSMO approximation. For data in COSMO, the V-shaped polyline is shifted down by about 5 kJ/mol relatively to the ordinate axis. At the same time, neutral films and films with $\alpha < 0.5$ in the aqueous phase are characterized by a slightly greater preference than half-protonated ones, while for gas-phase calculations the minimum $\Delta G^{Cl}/m$ falls precisely on films with $\alpha = 0.5$. Note that for carboxylic acids the character of the V-shaped broken line is similar to that of amines but with the preference for the formation of half-ionized monolayers, both in the gaseous and aqueous phases.[17] The obtained character of the change in $\Delta G^{Cl}/m$ shows that the process of dissociation or protonation of the surfactant aggregate will take place in the direction of reaching the structure corresponding to the minimum Gibbs energy, i.e., $\alpha = 0.5$. The advantage of structures with a neutral molecule−anion ratio of 1:1 and, most probably, also with a cation is confirmed by the available experimental data concerning the surface properties of soap foams with different alkyl chain lengths from 10 to 16 carbon atoms.[48−50]

Figure 4 shows the simplified scheme of protonation of an aggregate of m amine monomers. In the associate, protons are attached in such a way that, subsequently, when a monolayer is formed, the protonated and neutral molecules will be staggered. This is consistent with the above-described greater preference for such interactions. In this case, $m{\cdot}\alpha$ hydrogen ions are attached from the aqueous phase.

The derivation of the formula to calculate the equilibrium constant for the dissociation of carboxylic acids was described in detail in our recent work.[20] Since the protonation is the reverse process of the dissociation and their Gibbs energies are the same, but different in sign, here, we present only the final formula for calculation of the pK_b for amine monolayers

$$pK_b^{surf} = pK_b^{bulk} + 0.434\frac{\Delta G_{cat}^{Cl}/m - \Delta G_{neu}^{Cl}/m - \Delta G_{cat}^{solv} + \Delta G_{neu}^{solv}}{RT} \quad (4)$$

where pK_b^{bulk} is the pK_b value for amine monomers in water, ΔG_{neu}^{solv} and ΔG_{cat}^{solv} are the solvation Gibbs energies of the neutral and protonated monomers calculated in the aqueous phase, respectively, and $\Delta G_{neu}^{Cl}/m$ and $\Delta G_{cat}^{Cl}/m$ are the clusterization Gibbs energies per monomer for the neutral and half-protonated monolayer calculated in the gaseous phase, respectively.

It is obvious to see that the use of this formula connects the surface pK_b of the monolayer and bulk pK_b of monomers and allows an assessment without determination of the Gibbs energy in the formation of a solvated proton, which depends on the chosen experimental or theoretical technique.

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Notes

The authors declare no competing financial interest.

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