

## Section 3. Chemistry

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### THE INFLUENCE OF CERTAIN FUNCTIONAL GROUPS ON ADSORPTION PROCESSES AND MICELLE FORMATION IN AQUEOUS SOLUTIONS OF SURFACTANTS

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#### Abstract

This work investigates the processes of adsorption and micelle formation in aqueous solutions of surfactants (SAS), which determine their technological properties. Through theoretical analysis based on a method proposed in the literature, the contribution of various functional groups to the change in Gibbs free energy of these processes was assessed. The results show that the change in free energy during micelle formation can be represented as the sum of changes in energy of the hydrophilic and hydrophobic components of the SAS molecules. A linear dependence between the change in free energy and the number of hydrocarbon groups was revealed, allowing the calculation of the energetic contribution of a single hydrocarbon group. The analysis showed no direct dependence between the number of hydrophilic groups and the change in free energy, indicating that only a certain portion of these groups integrate into the micelles. The study also emphasizes the difference in the technological properties of solutions when using anionic surfactants and offers a new understanding of the thermodynamic aspects of adsorption and micelle formation processes in aqueous solutions of molecular SAS.

**Keywords:** *surfactants, adsorption, micelle formation, Gibbs free energy, functional groups, hydrophilic and hydrophobic components, technological properties*

#### Introduction

Within the framework of studying aqueous solutions of surfactants (SAS), in which the key roles are played by the processes of

adsorption and micelle formation, determining their technological properties, an analytical work aimed at evaluating the contribution of functional groups to the reduction of

Gibbs free energy in these processes was conducted. The analysis is based on a method mentioned in sources (Lin I.J., Marszall L., 1978; Maryaskin Y., Derman S., 2019), which allows for a first approximation to represent the change in Gibbs free energy during micelle formation as the sum of changes in energy for the hydrophilic and hydrophobic components of the SAS molecules:

$$\Delta G_m^0 = \Delta G_m^{0,P} + \Delta G_m^{0,R}, \quad (1)$$

where  $\Delta G_m^0$  denotes the change in Gibbs free energy upon forming micelles from one mole of SAS,  $\Delta G_m^{0,P}$  and  $\Delta G_m^{0,R}$  respectively reflect the changes in Gibbs energy for the hydrophilic and hydrophobic parts of the molecules.

### Research Part

In the context of the homologous series of SAS, the value of  $\Delta G_m^{0,P}$  is considered a constant, while  $\Delta G_m^{0,R}$  can be calculated as the change in free energy upon integrating one hydrocarbon group into the micelle ( $\Delta G_m^{CH_2}$ ), considering the number of such groups in the molecule (n) and Avogadro's number ( $N_A$ ).

From (1):

$$\Delta G_m^0 = \text{const} + n\Delta G_m^{CH_2} N_A, \quad (2)$$

From (2), it follows that in the coordinates  $\Delta G_m^0 - f(n)$  a linear dependence should be observed, where the slope of the line allows for the calculation of the change in free energy upon transitioning one hydrocarbon group into the micelle, and the segment cut off on the ordinate axis corresponds to the value of  $\Delta G_m^{0,P}$ .

Table 1 presents the calculated values of  $\Delta G_0$ ,  $\Delta G_m^{0,P}$  and  $\Delta G_m^{0,R}$  for a series of molecular SAS, using  $\Delta G_m^{0,P}$  values from (Lin I.J., 1972).

The presented data indicate that all values of  $\Delta G_m^{CH_2}$  are approximately the same (the average value of this magnitude is  $-5.64 \cdot 10^{-21}$  J). This value of  $\Delta G_m^{CH_2}$  was used in calculating  $\Delta G_m^{0,R}$  for the studied SAS.

It should be noted that our value of  $\Delta G_m^{CH_2}$  differs from those presented in (Maryaskin Y., Derman S., 2019; Maryaskin, Y.B., Danilov, F.I., 2004) for other classes of surfactant compounds. Likely, the nature of the hydrophilic parts of SAS affects the magnitude of this parameter.

Regarding the values of  $\Delta G_m^{0,P}$ , there is no correlation between the number of hydrophilic groups and the change in the system's

free energy. Likely, not all hydrophilic groups are integrated into the micelles, but only a certain part that ensures the maximum reduction of contact between the hydrocarbon radical and water. This limitation seems reasonable since the inclusion of hydrophilic groups in micelles is accompanied by an increase in Gibbs energy. Thus, the spontaneity of the micelle formation process in solutions of molecular SAS is conditioned by the fact that the absolute value of  $\Delta G_m^{0,R}$  is greater than  $\Delta G_m^{0,P}$ .

It should also be noted that, unlike the solutions mentioned, the use of anionic SAS is accompanied by a decrease in the value of  $\Delta G_m^{0,P}$ . Possibly, this is one of the reasons for the difference in the technological properties of these solutions.

The assumption that the properties of SAS molecules are composed of the properties of their hydrophilic and hydrophobic parts can also be applied to the adsorption process. In this case:

$$\Delta G_a^0 = \Delta G_a^{0,P} + \Delta G_a^{0,R}, \quad (3)$$

where  $\Delta G_a^0$  – is the change in free energy upon adsorbing one mole of SAS;  $\Delta G_a^{0,P}$  and  $\Delta G_a^{0,R}$  – are the changes in free energy upon adsorbing the hydrophilic and hydrophobic parts of SAS, respectively.

For the homologous series of SAS,  $\Delta G_a^{0,R}$  consists of the change in Gibbs free energy upon adsorbing one  $-CH_2-$  group of the hydrocarbon chain, considering their number in the molecule (n) and the number of molecules in one g-mole of adsorbate, and  $\Delta G_a^{0,P}$  is a constant magnitude:

$$\Delta G_a^0 = \text{const} + n\Delta G_a^{CH_2} N_A. \quad (4)$$

Values for the components of equation (4) are provided in Table 2. The calculations used of  $\Delta G_a^{0,P}$  values from (Lin I.J., 1972).

From this table, it is evident that all values  $\Delta G_a^{CH_2}$  are roughly the same (the average value of this magnitude is  $-4.19 \cdot 10^{-21}$  J). This value  $\Delta G_a^{CH_2}$  was used in calculating  $\Delta G_a^{0,R}$  for the studied SAS.

Regarding the magnitude of  $\Delta G_a^{0,P}$  – it is little dependent on the number of oxyethylene groups in the molecules of SAS. It can be assumed that approximately the same hydrophilic part of SAS molecules is placed at the phase boundary in all cases.

It is also worth noting that, unlike micelle formation, the adsorption of hydrophilic

groups of the studied SAS molecules is accompanied by a reduction in Gibbs free energy. This fact is what makes the adsorption process more thermodynamically favorable than micelle formation from a thermodynamic point of view.

Furthermore, it was shown in (Maslak, H. S., Maryaskin, 2023) that at the critical micelle concentration, the number of molecules that formed micelles is greater than those absorbed on the surface. There, it was also suggested that the presence of micelles in the solution volume might act as a barrier, hindering the delivery of molecules to the phase boundary, which affects the technological properties of SAS solutions.

### Conclusions

Thus, through the conducted study, the contribution of functional groups to the change in Gibbs free energy during adsorption and micelle formation in aqueous solutions of surfactants was assessed.

The analysis demonstrated that the change in free energy during micelle forma-

tion can be represented as the sum of changes in energy for the hydrophilic and hydrophobic parts of SAS molecules. The obtained data indicate a linear dependency between the change in free energy and the number of hydrocarbon groups in the molecule, confirming the significance of hydrophobic interactions in the process of micelle formation.

It was also established that the magnitude of the change in free energy for hydrophilic groups does not show a direct correlation with their number, indicating the selective inclusion of these groups into micelles. The results emphasize the thermodynamic advantage of adsorption compared to micelle formation and suggest that the presence of micelles in the solution might affect the technological properties of SAS by limiting the delivery of molecules to the phase boundary.

Thus, the study provides new insights into the thermodynamic aspects of SAS behavior in aqueous solutions, important for understanding and optimizing their technological applications.

**Table 1.** Values of  $\Delta G_m^{CH_2}$ ,  $\Delta G_m^{O,R}$  and  $\Delta G_m^{O,P}$  for molecular surfactants ( $T=298$ )

Surfactant formula	Dependency equation $\Delta G_m^0 - f(n)$	$\Delta G_m^{CH_2} * 10^{21}$ , J	$\Delta G_m^{O,R} * 10^{-3}$ , J/mol	$\Delta G_m^{O,P} * 10^{-3}$ , J/mol
$C_8H_{17}O(C_2H_4O)_3H$			-27.16	
$C_{10}H_{21}O(C_2H_4O)_3H$	$\Delta G_m^0 = 1850 - 3210n$	- 5.33	-33.95	1.85
$C_{12}H_{25}O(C_2H_4O)_3H$			-40.74	
$C_8H_{17}O(C_2H_4O)_6H$			-27.16	
$C_{10}H_{21}O(C_2H_4O)_6H$	$\Delta G_m^0 = 6960 - 3510n$	-5.83	-33.95	6.96
$C_{12}H_{25}O(C_2H_4O)_6H$			-40.74	
$C_8H_{17}O(C_2H_4O)_8H$			-27.16	
$C_{12}H_{25}O(C_2H_4O)_8H$	$\Delta G_m^0 = 7569.3 - 3509.6n$	-5.83	-40.74	7.57
$C_{14}H_{29}O(C_2H_4O)_8H$			-47.53	
$C_8H_{17}O(C_2H_4O)_{10}H$			-27.16	
$C_{10}H_{21}O(C_2H_4O)_{10}H$	$\Delta G_m^0 = 6060 - 3280n$	-5.45	-33.95	6.06
$C_{12}H_{25}O(C_2H_4O)_{10}H$			-40.74	
$C_{14}H_{29}O(C_2H_4O)_{10}H$			-47.53	
$C_8H_{17}O(C_2H_4O)_{12}H$			-27.16	
$C_{10}H_{21}O(C_2H_4O)_{12}H$	$\Delta G_m^0 = 6933 - 3375.5n$	-5.61	-33.95	6.93
$C_{12}H_{25}O(C_2H_4O)_{12}H$			-40.74	
$C_{14}H_{29}O(C_2H_4O)_{12}H$			-47.53	
$C_8H_{17}O(C_2H_4O)_{14}H$			-27.16	
$C_{12}H_{25}O(C_2H_4O)_{14}H$	$\Delta G_m^0 = 9280 - 3480n$	-5.78	- 40.74	9.28
$C_{14}H_{29}O(C_2H_4O)_{14}H$			- 47.53	

**Table 2.** Values of  $\Delta G_a^{CH_2}$ ,  $\Delta G_a^{0,R}$  and  $\Delta G_a^{0,P}$  for molecular surfactants ( $T=298$ )

Surfactant formula	Dependency equation $\Delta G_a^0 - f(n)$	$\Delta G_a^{CH_2} * 10^{21}$ , J	$\Delta G_a^{0,R} * 10^{-3}$ , J/mol	$\Delta G_a^{0,P} * 10^{-3}$ , J/mol
$C_8H_{17}O(C_2H_4O)_3H$			-20.18	
$C_{10}H_{21}O(C_2H_4O)_3H$	$\Delta G_a^0 = -21547 - 2375n$	-3.94	-25.22	-21.55
$C_{12}H_{25}O(C_2H_4O)_3H$			-30.27	
$C_8H_{17}O(C_2H_4O)_6H$			-20.18	
$C_{10}H_{21}O(C_2H_4O)_6H$	$\Delta G_a^0 = -20258 - 2437.5n$	-4.05	-30.27	-20.26
$C_{12}H_{25}O(C_2H_4O)_6H$			-35.31	
$C_8H_{17}O(C_2H_4O)_8H$			-20.18	
$C_{12}H_{25}O(C_2H_4O)_8H$	$\Delta G_a^0 = -15371 - 2854.6n$	-4.74	-30.27	-15.37
$C_{14}H_{29}O(C_2H_4O)_8H$			-35.31	
$C_8H_{17}O(C_2H_4O)_{10}H$			-20.18	
$C_{10}H_{21}O(C_2H_4O)_{10}H$	$\Delta G_a^0 = -20149 - 2546n$	-4.23	-25.22	-20.15
$C_{12}H_{25}O(C_2H_4O)_{10}H$			-30.27	
$C_{14}H_{29}O(C_2H_4O)_{10}H$			-35.31	
$C_8H_{17}O(C_2H_4O)_{12}H$			-20.18	
$C_{10}H_{21}O(C_2H_4O)_{12}H$	$\Delta G_a^0 = -18716 - 2591.5n$	-4.30	-25.22	-18.72
$C_{12}H_{25}O(C_2H_4O)_{12}H$			-30.27	
$C_{14}H_{29}O(C_2H_4O)_{12}H$			-35.31	
$C_8H_{17}O(C_2H_4O)_{14}H$			-20.18	
$C_{12}H_{25}O(C_2H_4O)_{14}H$	$\Delta G_a^0 = -21730 - 2325n$	-3.86	-30.27	-21.73
$C_{14}H_{29}O(C_2H_4O)_{14}H$			-35.31	

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