

Section 2. Chemistry

DOI:10.29013/ESR-23-9.10-7-12



INFLUENCE OF MICELLAR STRUCTURES ON THE ADSORPTION CAPACITY OF SURFACTANTS

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Cite: Maslak, H.S., Maryaskin, Y.B., Derman S. (2023). *Influence of Micellar Structures on the Adsorption Capacity of Surfactants*. *European Science Review 2023, No 9–10*. <https://doi.org/10.29013/ESR-23-9.10-7-12>

Abstract

This paper continues the study of the adsorption properties of surfactants (surfactants) in aqueous solutions, with particular attention to the influence of micellar structures. The central theme of the study is to analyze the interaction between adsorption and micelle formation, and their influence on the technological properties of surfactants. The study details the thermodynamic and kinetic aspects of these processes, highlighting changes in Gibbs free energy and surface tension. Based on quantitative data, the paper demonstrates how the relationship between adsorption and micelle formation depends on the surfactant concentration in the solution. The results highlight the importance of an integrated approach to study surfactants and optimize their use in applications ranging from water purification to detergent development.

Keywords: *surfactants, adsorption, micelle formation, aqueous solutions, Gibbs free energy, surface tension, thermodynamics, kinetics*

Introduction

This article presents a continuation of our previous research cycle devoted to the study of adsorption properties of surfactants (surfactants) in aqueous solutions. Particular attention is given to analysing the influence of micellar structures on the adsorption efficiency of surfactants, which is a key factor in many technological and environmental pro-

cesses. Our previous publications in this field (Maryaskin & Derman, 2019; Maryaskin & Derman, 2021) focused on basic aspects of adsorption and micelle formation, emphasizing the importance of an integrated approach to the study of these phenomena.

We further extend this analysis by considering both thermodynamic and kinetic aspects of the interaction between adsorption

and micelle formation in the surfactant aqueous solution system. Building on previous work, we deepen our understanding of the mechanisms governing these processes and their influence on the technological properties of surfactants, including changes in Gibbs free energy and surface tension. The aim of this paper is to extend the theoretical framework, with the aim of optimising the use of surfactants in a variety of industries, from water treatment to the development of new detergents.

Adsorption of surfactants (surfactants), from aqueous media at various interfaces, is an important factor determining the efficiency of the technological properties of these solutions (ability to remove contaminants, emulsification, dispersion, etc.).

There are many theories devoted to the description of the adsorption process (Adams, 1979; Hiemenz, & Rajagopala, 1997). However, these theories do not consider the fact that in aqueous solutions of surfactants, in addition to adsorption, the process of micelle formation can take place. In Maryaskin and Derman (2019) it is suggested that these simultaneous processes mutually influence each other. The present work is devoted to an attempt to consider such influence.

Consider a system consisting of an aqueous surfactant solution. Due to the specificity of its properties, some surfactants participate in the processes of adsorption and micelle formation, i.e., the initial number of

individual surfactant particles in the solution volume decreases. Let us introduce the following notations:

τ – time to reach the equilibrium of adsorption and micelle formation processes.

c_0 – initial concentration of surfactant in the solution volume.

c – concentration of individual surfactants in the solution volume after adsorption and micelle formation.

During the time τ the concentration of individual surfactants in the solution volume decreased by $c_0 - c$:

$$\frac{dc}{d\tau} = c_0 - c \quad (1)$$

where $c_0 - c$ is the amount of surfactants adsorbed on the surface and grouped into micelles.

Let us denote by α the fraction, from $c_0 - c$, of surfactants adsorbed, and by β the fraction of surfactants that have formed micelles:

$$\frac{dc}{d\tau} = (c_0 - c)\alpha + (c_0 - c)\beta \quad (2)$$

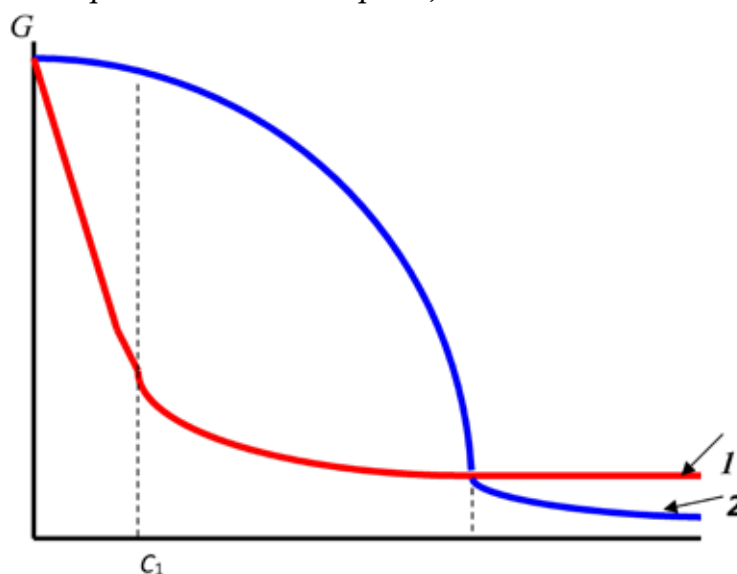
From (2), dividing the variables, we obtain:

$$\int_{c_0}^{c_0-c} \frac{dc}{c_0 - c} = \alpha \int_0^\tau d\tau + \beta \int_0^\tau d\tau \quad (3)$$

Applying the substitution method, from (3) we obtain:

$$c = c_0(1 - e^{-(\alpha+\beta)\tau}) \quad (4)$$

Figure 1. Scheme of Gibbs free energy change in the processes: 1 – adsorption; 2 – micellization



At low concentrations of surfactants in solution, surface-active particles easily reach the interface and adsorb on it. In this case $\alpha \gg \beta$ and the decrease in the amount of individual surfactants in the solution volume is mainly due to the adsorption process:

$$c = c_0(1 - e^{-\alpha t}) \quad (5)$$

Accordingly, this spontaneous process is accompanied by a decrease in the Gibbs free energy (G). From Figure 1, this state of the system is maintained up to a surfactant concentration equal to C_1 .

As the surfactant concentration increases in the solution volume, the probability of surface-active particles colliding with each other increases. In this case, it is difficult for surfactant particles to reach the interface surface and the probability of their adsorption decreases. At the same time, the probability of aggregation of surfactant particles into micelles increases. In this case, the decrease in the Gibbs free energy is due to the simultaneous occurrence of two processes: adsorption and micelle formation. From (Figure 1), such a state of the system takes place in the interval of surfactant concentrations between C_1 and C_k .

As is known, at the surfactant concentration in solution equal to the critical micelle formation concentration (C_k), intensive micelle formation is observed, and adsorption reaches its practically constant value. In this case, further decrease in the number of individual surface-active particles in the volume, is mainly due to their micelle formation and hence $\beta \gg \alpha$. Such a state corresponds to the section of (Figure 1), at concentrations higher than C_k .

Further, even though adsorption attributed to one mole of surfactant is energetically more favourable than micelle formation (Maryaskin & Derman, 2019), the second process, which involves many particles, occurs predominantly.

Let us consider the proposed scheme from the point of view of the laws of thermodynamics.

For an aqueous surfactant solution, the relationship between the isobaric-isothermal potential at adsorption and the chemical potential of the surface-active component, considering the interface area, is described by the equation (Hiemenz & Rajagopala, 1997):

$$G_{ads} = \sigma s + \mu_{ads} n_{ads} \quad (6)$$

where G_{ads} – surface Gibbs free energy at adsorption, σ – surface tension of solution; s – surface area of interface; μ_{ads} – chemical potential of surface-active component at adsorption; n_{ads} – number of moles of adsorbed surface-active component.

As a result of adsorption there is a decrease in the surface tension at the interface between air and solution. This decrease continues up to the surfactant concentration in the solution, equal to the critical concentration of micelle formation (C_k), at which the surface tension reaches its minimum, constant in a certain range of concentrations, value (σ_{min}).

According to our assumption, this state can be influenced by the process of aggregation of surfactants into micelles, occurring in the solution volume.

According to Hill (2001), micellar structure can be considered as a system consisting of many nanoparticles distributed in a liquid medium. The thermodynamics of a system consisting of N identical spherical nanoparticles (micelles), with the average number of surfactant moles in each micelle equal to n_{mic} , was considered in Hill (1963) and Chamberlin (2015).

In the first approximation, the Gibbs energy of micelle formation is equal to:

$$G_{mic} = \mu_{mic} n_{mic} + NW \quad (7)$$

where μ_{mic} – chemical potential of the surface-active component during micelle formation; W – value introduced for nanoparticles and characterized as the work of interfacial boundary formation (in this case, the micelle-solution interface).

As noted earlier, when C_k is reached, the free energies of adsorption and micelle formation processes are equal to each other. In this case, from (6), (7) we obtain, taking the interface area as a unit:

$$\sigma_{min} = \mu_{mic} n_{mic} - \mu_{ads} n_{ads} + NW \quad (8)$$

From (8) it can be seen that the value σ_{min} achieved in aqueous solutions with surfactant concentration equal to C_k is the resultant of two processes: adsorption and micelle formation. This value remains almost constant with some increase in surfactant concentration. According to (8), it is possible at insignificant change of all parameters of the system. However, further increase in surfactant concentration often leads to the destruction of micellar

structures, which is again accompanied by a decrease in surface tension.

Using the data given in Maryaskin and Derman (2019) on the change of Gibbs free energy during adsorption of one mole of surfactant (ΔG_{ads}^0) attributed to the surface unit, the change of this energy for surfactant in the amount equal to A_∞ was calculated:

$$\Delta G_{ads} = \Delta G_{ads}^0 \times A_\infty \quad (9)$$

where A_∞ is the limiting adsorption achieved at the critical concentration of micelle formation, ΔG_{ads}^0 is the change in Gibbs energy during adsorption of surfactant in an amount equal to A_∞ .

Further, using the data on the Gibbs free energy change during micelle formation of one mole of surfactant (ΔG_{mic}^0) (Maryaskin & Derman, 2019), and the assumption that at C_k the equality between the reduction of free energies of adsorption and micelle formation processes is reached, the number of surfactant moles participating in micelle formation Σn_{mic} was calculated:

$$\Sigma n_{mic} = \Delta G_{ads} \div \Delta G_{mic}^0 \quad (10)$$

The value of Σn_{mic} per unit volume of solution is equal to the concentration of surfactants forming micelles, C_{mic} (mol/m³).

The total concentration of surfactants adsorbed and formed micelles (C_{tot}) is:

$$C_{tot} = A_\infty + C_{mic} \quad (11)$$

The results of the calculations are given in Tables 1, 2. It follows from these data that the amount of surfactants grouped into micelles in all cases is greater than that adsorbed on the surface. Also note that in the processes of adsorption and micelle formation participate only a small part of the total amount of surface-active particles ($C_{tot} \ll C_k$). However, it should be considered that in technological processes, as a rule, solutions with surfactant concentration several times higher than the critical concentration of micelle formation are used. In this case, the value of C_{tot} will be larger than shown in the tables.

Table 1. Amounts of adsorbed and micelle-forming molecular surfactants ($T = 288\text{ K}$)

Substance formula	$\Delta G_{ads}^0 \cdot 10^{-3}$, J/mol *	$\Delta G_{mic}^0 \cdot 10^{-3}$, J/mol *	C_k , mol/m ³ *	D	$A_\infty \cdot 10^6$, mol/m ²	$C_{mic} \cdot 10^6$, mol/m ³	$C_{tot} \cdot 10^6$, mol/m ³
$C_8H_{17}O(C_2H_4O)_3H$	-35.90	-21.10	8.214	-0.075	2.09	3.55	5.64
$C_{10}H_{21}O(C_2H_4O)_3H$	-43.87	-26.84	0.744	-0.110	2.51	4.10	6.61
$C_{12}H_{25}O(C_2H_4O)_3H$	-45.47	-34.46	0.031	-0.171	3.76	4.96	8.72
$C_8H_{17}O(C_2H_4O)_6H$	-40.09	-20.10	12.59	-0.067	1.67	3.33	5.0
$C_{10}H_{21}O(C_2H_4O)_6H$	-43.56	-25.41	1.36	-0.091	2.09	3.58	5.67
$C_{12}H_{25}O(C_2H_4O)_6H$	-47.86	-32.06	0.084	-0.120	2.51	3.75	6.26
$C_8H_{17}O(C_2H_4O)_8H$	-35.30	-18.93	20.40	-0.059	1.67	3.11	4.78
$C_{12}H_{25}O(C_2H_4O)_8H$	-49.30	-31.41	0.11	-0.103	2.09	3.28	5.37
$C_{14}H_{29}O(C_2H_4O)_8H$	-49.95	-37.49	0.0087	-0.167	3.34	4.45	7.79
$C_8H_{17}O(C_2H_4O)_{10}H$	-44.68	-17.63	35.74	-0.056	1.25	3.16	4.41
$C_{10}H_{21}O(C_2H_4O)_{10}H$	-50.26	-25.17	1.49	-0.063	1.25	2.49	3.74
$C_{12}H_{25}O(C_2H_4O)_{10}H$	-44.99	-30.62	0.12	-0.094	2.09	3.07	5.16
$C_{14}H_{29}O(C_2H_4O)_{10}H$	-58.87	-37.14	0.01	-0.123	2.09	3.31	5.40
$C_8H_{17}O(C_2H_4O)_{12}H$	-42.29	-17.51	37.74	-0.053	1.25	3.02	4.27
$C_{10}H_{21}O(C_2H_4O)_{12}H$	-41.88	-24.87	1.69	-0.070	1.67	2.81	4.48
$C_{12}H_{25}O(C_2H_4O)_{12}H$	-44.51	-29.19	0.144	-0.093	2.09	3.19	5.28
$C_{14}H_{29}O(C_2H_4O)_{12}H$	-50.26	-37.03	0.01	-0.126	2.51	3.41	5.92
$C_8H_{17}O(C_2H_4O)_{14}H$	-39.01	-17.30	41.35	-0.049	1.25	2.82	4.07
$C_{12}H_{25}O(C_2H_4O)_{14}H$	-51.45	-29.47	0.25	-0.086	1.67	2.91	4.58
$C_{14}H_{29}O(C_2H_4O)_{14}H$	-52.17	-36.73	0.012	-0.109	2.09	2.97	5.06

* Maryaskin & Derman (2019)

Table 2. Amounts of adsorbed and micelle-forming molecular surfactants ($T = 298\text{ K}$)

Substance formula	$\Delta G_{\text{ads}}^0 \cdot 10^{-3}$ J/mol *	$\Delta G_{\text{mic}}^0 \cdot 10^{-3}$ J/mol *	C_k^* mol/m ³ *	D	$A_{\infty} \cdot 10^6$ mol/m ²	$C_{\text{mic}} \cdot 10^6$ mol/m ³	$C_{\text{tot}} \cdot 10^6$ mol/m ³
$C_8H_{17}O(C_2H_4O)_3H$	-41.08	-24.57	5.52	-0.0797	1.94	3.24	5.18
$C_{10}H_{21}O(C_2H_4O)_3H$	-44.23	-28.77	0.49	-0.118	2.66	4.10	6.76
$C_{12}H_{25}O(C_2H_4O)_3H$	-50.58	-37.41	0.015	-0.159	3.15	4.25	7.40
$C_8H_{17}O(C_2H_4O)_6H$	-40.23	-22.08	7.48	-0.070	1.74	3.17	4.91
$C_{10}H_{21}O(C_2H_4O)_6H$	-43.69	-27.52	0.83	-0.093	2.14	3.40	5.54
$C_{12}H_{25}O(C_2H_4O)_6H$	-49.48	-36.32	0.24	-0.140	2.83	3.85	6.68
$C_8H_{17}O(C_2H_4O)_8H$	-38.00	-20.61	13.49	-0.061	1.61	2.96	4.57
$C_{12}H_{25}O(C_2H_4O)_8H$	-50.25	-34.24	0.055	-0.109	2.18	3.18	5.36
$C_{14}H_{29}O(C_2H_4O)_8H$	-54.92	-41.77	0.026	-0.158	2.87	3.78	6.65
$C_8H_{17}O(C_2H_4O)_{10}H$	-42.23	-20.56	13.76	-0.054	1.29	2.63	3.92
$C_{10}H_{21}O(C_2H_4O)_{10}H$	-43.98	-27.52	0.83	-0.080	1.82	2.91	4.73
$C_{12}H_{25}O(C_2H_4O)_{10}H$	-48.82	-30.60	0.063	-0.089	1.82	2.91	4.73
$C_{14}H_{29}O(C_2H_4O)_{10}H$	-57.59	-41.40	0.003	-0.131	2.26	3.16	5.42
$C_8H_{17}O(C_2H_4O)_{12}H$	-39.11	-19.44	21.59	-0.0536	1.37	2.76	4.13
$C_{10}H_{21}O(C_2H_4O)_{12}H$	-44.74	-27.80	0.74	-0.076	1.70	2.73	4.43
$C_{12}H_{25}O(C_2H_4O)_{12}H$	-50.61	-33.51	0.074	-0.096	1.90	2.86	4.76
$C_{14}H_{29}O(C_2H_4O)_{12}H$	-54.43	-40.04	0.0053	-0.134	2.46	3.32	5.78
$C_8H_{17}O(C_2H_4O)_{14}H$	-40.36	-18.56	30.86	-0.049	1.21	2.64	3.85
$C_{12}H_{25}O(C_2H_4O)_{14}H$	-49.54	-32.48	0.11	-0.090	1.82	2.77	4.59
$C_{14}H_{29}O(C_2H_4O)_{14}H$	-54.34	-39.44	0.0072	-0.125	2.30	3.17	5.47

* Maryaskin & Derman (2019)

As noted, the use of surfactants in technological processes is associated with their adsorption activity at the corresponding interfaces. It can be assumed that the presence of many micelles in the volume will affect the technological properties of surfactant solutions, for example, the rate of delivery of surface-active particles to the treated surfaces.

This, in particular, is shown in Maryaskin and Derman (2021), on the example of the use in the washing process of two molecular surfactants with approximately the same adsorption characteristics. Nevertheless, the cleaning rate in these micellar solutions differs significantly, which may be related to the above-mentioned kinetic factor.

All of the above reveals a complex relationship between adsorption and micelle formation. The paper emphasizes that in aqueous surfactant solutions these two processes not only occur in parallel but also mutually influence each other, which is important for understanding their technological characteristics.

The key point is the finding that at low surfactant concentrations adsorption dominates, while with increasing concentration there is a transition to the predominance of micelle formation. This accounts for changes in the Gibbs free energy and surface tension of the solution. Especially significant is the establishment of the critical concentration of micelle formation (C_k), at which the minimum of surface tension is reached.

The results of the study show that adsorption and micelle formation are complementary processes, and their ratio depends on the initial concentration of surfactant in the solution. It is also observed that only a fraction of surfactant particles is involved in the adsorption and micelle formation processes.

This has important practical implications for the application of surfactants in various technological processes such as cleaning, emulsification, and dispersion. Understanding the mechanisms of interaction between adsorption and micelle formation can facilitate

the development of more efficient and targeted surfactant applications in industry.

The authors plan to further discuss this topic in their next publication.

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submitted 29.11.2023;

accepted for publication 03.12.2023;

published 26.01.2024

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