

Section 6. Chemistry

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EFFECT OF BULK MICELLIZATION ON THE REDUCTION OF SURFACE TENSION IN AQUEOUS SURFACTANT SOLUTIONS

Derman S.¹, Maryaskin Y. B.², Maslak H. S.², Netronina O.²

¹ Senior Electrochemical Technologies Researcher, Addionics Ltd., Israel

² Department of Biochemistry and Medical Chemistry,
Dnipro State Medical University, Ukraine

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Abstract

This study considers the possible effect of micellization in the bulk solution on the reduction of surface tension in aqueous surfactant solutions. Based on the Langmuir adsorption model and the Szyszkowski equation, the dependences of surface tension on concentration were analyzed for a number of surfactants.

It is shown that, for some of the systems considered, before the critical micelle concentration is reached, the dependence of the change in surface tension on $\ln C$ is close to linear, while the calculated surface coverage at the CMC is 95,2–100%. For some ionic surfactants, deviation from linearity is observed even before the CMC is reached. It is assumed that such behavior may be associated with premicellar association of surfactant molecules and a decrease in the fraction of monomeric forms directly available for adsorption. At higher concentrations, the subsequent change in surface tension may be associated with structural reorganization of micellar aggregates and a change in the nature of their growth.

The results obtained show that, when considering the adsorption properties of surfactant solutions, it is necessary to take into account not only the state of the surface layer but also the association processes occurring in the bulk solution.

Keywords: *surfactants, adsorption, micellization, critical micelle concentration, Langmuir isotherm, Szyszkowski equation, surface tension*

1. Introduction

As is well known, two spontaneous processes may occur in aqueous surfactant solutions: adsorption at the phase interface and

micellization in the bulk aqueous phase (Adamson A., 1979). In one of our previous studies, we suggested that these processes mutually influence the surface tension attained in

these solutions (Maruaskin Y., Derman S., 2019).

The effect of micellization on the adsorption characteristics of aqueous surfactant solutions should also be considered from a thermodynamic standpoint, based on the change in the chemical potential of monomeric surfactant forms in the bulk solution. Micelle formation does not imply direct displacement of surfactant molecules from the phase interface; however, upon reaching the critical micelle concentration, the activity of the monomeric forms changes much more slowly, which limits the further increase in surface adsorption and promotes stabilization of surface tension (Adamson A. W., Gast A. P., 1997; Rosen M. J., Kunjappu J. T., 2012; Tanford C., 1980).

In accordance with this assumption, the concept of the probability of occurrence of these processes was introduced (Maslak H. S., Maryaskin Y. B., Derman S., 2023). It was assumed that, at low concentrations, surfactant particles readily reach the interface and the adsorption process predominates. As the amount of surfactant in the bulk solution increases, the distance between individual particles decreases, the probability of their aggregation into micelles increases and, accordingly, the probability of adsorption decreases. Ultimately, adsorption reaches a constant value. According to (Fridrikhsberg D. A., 1974), this is observed at a surfactant concentration equal to the critical micelle concentration, C_k .

The concept of the probability of adsorption and aggregation used below is phenomenological and reflects the competition between the transport of surfactant molecules to the phase interface and their association in the bulk solution. In a thermodynamic approximation, such competition can be considered as a redistribution of monomeric surfactant forms between the surface layer and the bulk solution as their chemical potential changes (Rosen M. J., Kunjappu J. T., 2012; Myers D., 2006).

2. Theoretical Background and Calculation Method

Let us consider the above using the principles of Langmuir adsorption theory (Fridrikhsberg D. A., 1974). It should be taken into

account that this theory originally considered reversible adsorption at adsorption sites on the surface of solid particles. In the case of the solution-air interface, however, the liquid surface is homogeneous, and adsorption can occur on any free area of the surface.

It should be noted that applying the Langmuir isotherm to surfactant adsorption at the solution-air interface is an approximation. Unlike solid surfaces, the liquid-gas interface does not contain fixed adsorption sites, and lateral interactions between adsorbed molecules are possible in the surface layer. Nevertheless, in the range of moderate surfactant concentrations and in the absence of pronounced interactions, the Langmuir isotherm is widely used to estimate adsorption parameters (Adamson A. W., Gast A. P., 1997; Rosen M. J., Kunjappu J. T., 2012).

Let the total area of the air-solution interface be taken as unity, and let S denote the surface area occupied by the adsorbate. The surface area free of adsorbate will then be equal to $1 - S$.

According to the theory under consideration, adsorption is a reversible process, that is, at equilibrium the adsorption and desorption rates are equal.

In this case:

$$S = KC/(KC + 1) \quad (1)$$

where K is the adsorption equilibrium constant and C is the surfactant concentration in the solution.

The Szyszkowski equation, derived using the principles of Langmuir theory (Fridrikhsberg D. A., 1974), can be used to determine the adsorption characteristics of the process. According to this equation, up to the critical micelle concentration, a linear dependence should be observed in the coordinates $\sigma_0 - \sigma = f(\ln C)$, where σ_0 is the surface tension of the solvent (water) and σ is the surface tension of the surfactant solution.

The Szyszkowski equation used here is related to the fundamental Gibbs adsorption equation and makes it possible to estimate the adsorption characteristics of the system from the change in surface tension with concentration. For real surfactants, especially ionic ones, such treatment should be regarded as approximate and applied within the concentration range in which the selected linear dependence is experimentally

observed (Adamson A. W., Gast A. P., 1997; Rosen M. J., Kunjappu J. T., 2012).

According to the Szyszkowski equation, the limiting adsorption (A_∞) can be calculated from the plot of $\sigma_0 - \sigma$ versus $\ln C$ using the tangent of the slope angle of the straight line (α):

$$\operatorname{tg} \alpha = A_\infty RT \quad (2)$$

where R is the gas constant and T is the temperature.

The adsorption equilibrium constant can be determined from the same plot using the intercept (a) cut off by the straight line on the ordinate axis:

$$a = A_\infty RT \ln K \quad (3)$$

After determining A_∞ and K , the surface area occupied by the adsorbate can be calculated using equation (1).

3. Results and Discussion

In the reasoning presented above, it is assumed that, up to C_k , either only the adsorption process occurs in the solution or micellization has little effect on this process. Figures 1 and 2 show that such an almost linear dependence of $\sigma_0 - \sigma$ on $\ln C$ is observed in a number of surfactant solutions.

Figure 1. Dependence of $\sigma_0 - \sigma$ on $\ln C$ for $C_{14}H_{29}O(C_2H_4O)_8H$, $T = 298\text{ K}$

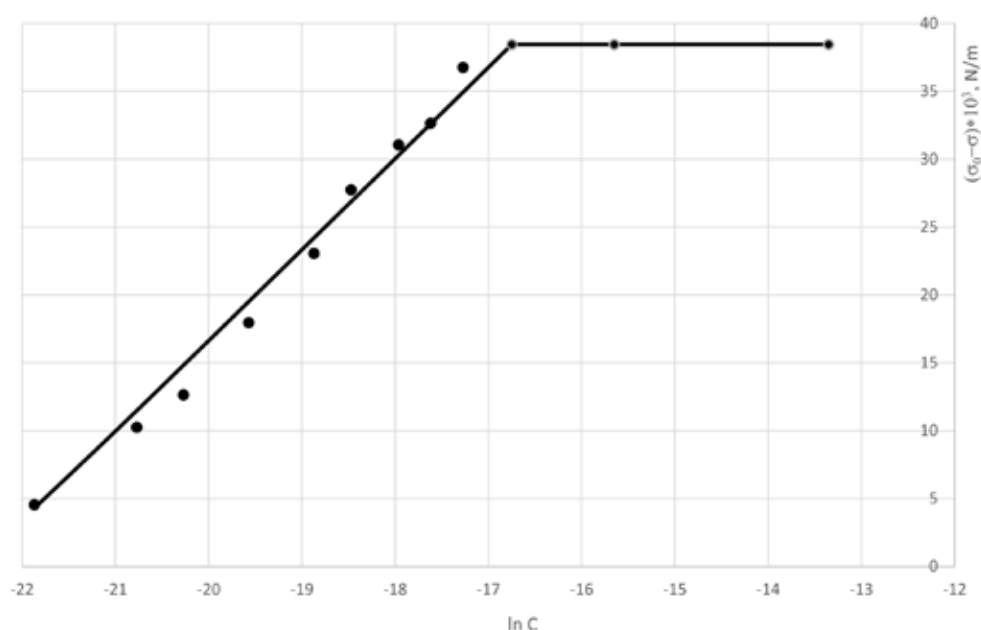
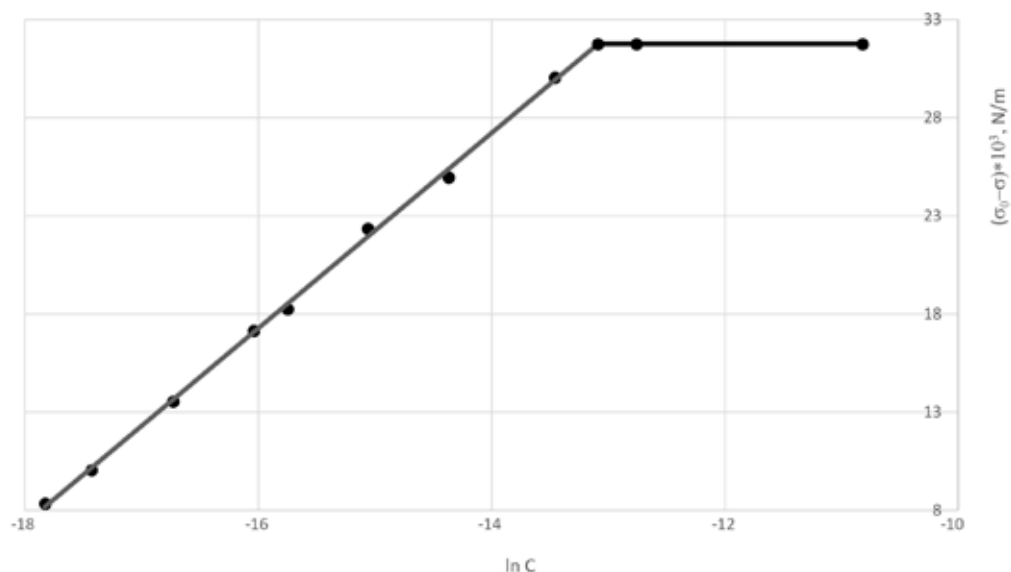


Figure 2. Dependence of $\sigma_0 - \sigma$ on $\ln C$ for $C_{12}H_{25}O(C_2H_4O)_{10}H$, $T = 293\text{ K}$



The adsorption characteristics of these solutions, calculated using the equations given above, are presented in Table 1.

Table 1. Adsorption characteristics of surfactant solutions

Surfactant	Ck, mole fraction	K	S, %	T, K
$C_{12}H_{25}O(C_2H_4O)_{10}H$	$2,07 \times 10^{-6}$	$3,2 \times 10^8$	99,8	293
$C_{14}H_{29}O(C_2H_4O)_8H$	$5,32 \times 10^{-8}$	$17,19 \times 10^9$	100	298

As follows from the data obtained, in the solutions presented, when Ck is reached, the surface is almost completely covered with surfactant particles. With a further increase in concentration, micellization becomes intensive.

Before the CMC is reached, monomeric surfactant forms predominate in the solution, while the contribution of associated particles to the thermodynamic characteristics of the system generally remains relatively small. Therefore, within this concentration range, adsorption at the phase interface may remain the dominant process, which is manifested in the nearly linear dependence of surface tension on the logarithm of concentration (Rosen M. J., Kunjappu J. T., 2012; Myers D., 2006).

3.1. Deviation from Linearity and the Effect of Micellar Aggregation

However, the linear character of the dependence of $\sigma_0 - \sigma$ on $\ln C$ is not observed in all cases.

For example, as follows from Figures 3 and 4, in solutions of sodium dodecyl sulfate and sodium 4-hexadecyl sulfate, some deviation from linearity is observed even before Ck is reached. This may be associated with an increase in the probability of surfactant aggregation into micelles, which should reduce the rate of surfactant adsorption. Extrapolation of the linear section of the dependence of $\sigma_0 - \sigma$ on $\ln C$ shows that, if only an unhindered adsorption process occurred, the surface tension attained at Ck should be reached at a lower amount of surfactant (Figs. 3, 4). At the same time, in the case of sodium 4-hexadecyl sulfate, almost complete surface coverage by the adsorbate is retained (Table 2). Presumably, in this example micellization only slightly retards the transfer of surfactant to the surface.

Deviation from linearity at concentrations below the CMC may be associated not only with the formation of fully developed micelles, but also with premicellar association of surfactant molecules, the formation of dimers and oligomeric associates, as well as with enhanced lateral interactions in the surface layer. These effects reduce the fraction of monomeric surfactant forms directly available for adsorption and thereby may decrease the rate of further reduction in surface tension (Rosen M. J., Kunjappu J. T., 2012; Israelachvili J. N., 2011; Myers D., 2006).

In the case of sodium dodecyl sulfate, a somewhat lower degree of surface coverage by the adsorbate is reached at Ck (Table 2). It can be assumed that aggregation of particles into micelles constitutes a certain barrier that prevents attainment of adsorption equilibrium.

In this case, aggregation of surfactant molecules in the bulk solution can be regarded as a factor limiting attainment of adsorption equilibrium through a change in monomer activity. Such behavior may lead to a temporary slowdown in the increase in surface adsorption and may appear as inflections or plateaus in the concentration dependence of surface tension.

3.2. Structural Reorganization of Micelles and the Second Critical Concentration

With a further increase in concentration, a repeated change in the character of the surface-tension dependence should not be unambiguously associated with the destruction of spherical micelles. In a number of systems, it may be accompanied by a change in the growth regime and structural organization of micellar aggregates. The transition from relatively weak to more intensive micelle growth is regarded in the literature as one of the manifestations of the second crit-

ical micelle concentration, $C_{k,2}$ (Porte G., Poggi Y., Appell J., Maret G., 1984; Bergström L. M., 2016). Therefore, the observed further decrease in surface tension should be interpreted as a possible consequence of reorganization of the micellar system and the corresponding change in the equilibrium among monomeric surfactant forms, aggregates, and the surface layer.

Depending on the nature of the surfactant and the solution composition, such structural reorganization may be accompanied by the formation of elongated or other nonspherical aggregates; however, establishing the specific morphology for the systems considered requires independent structural confirmation (Bergström L. M., 2016).

Early studies by K. Shinoda and co-authors demonstrated a substantial dependence of the critical micelle concentration, micelle aggregation characteristics, and self-organization processes on solution composition and the presence of electrolytes and organic additives (Shinoda K., 1954; Shinoda K., Nakagawa T., Tamamushi B., Isemura T., 1963; Shinoda K., 1954). These results are of historical and experimental interest in the context of the subsequent development of concepts concerning the structural evolution of micellar systems, whereas direct discussion of the second CMC is more appropriately associated with later studies (Porte G., Poggi Y., Appell J., Maret G., 1984; Bergström L. M., 2016).

Figure 3. Dependence of $\sigma_0 - \sigma$ on $\ln C$ for sodium 4-hexadecyl sulfate, $T = 20^\circ \text{C}$

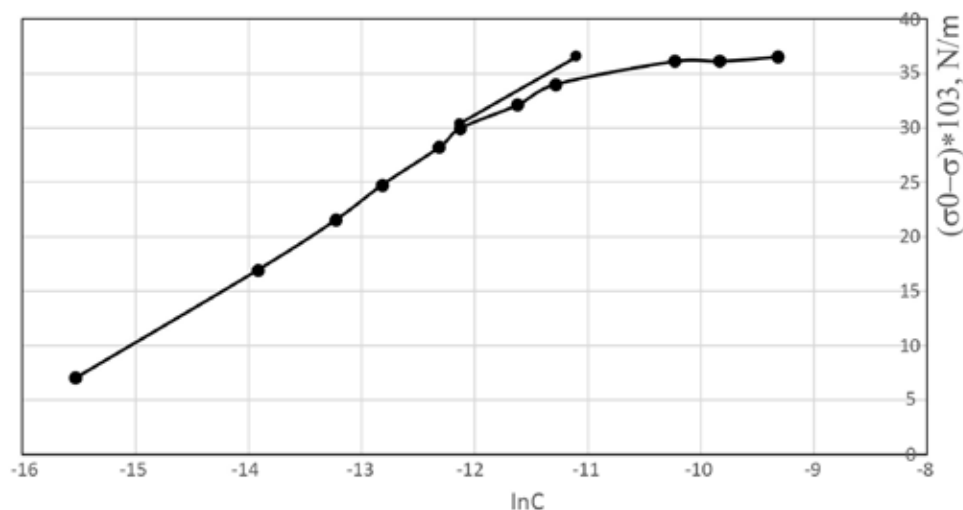


Figure 4. Dependence of $\sigma_0 - \sigma$ on $\ln C$ for sodium dodecyl sulfate, $T = 293 \text{ K}$

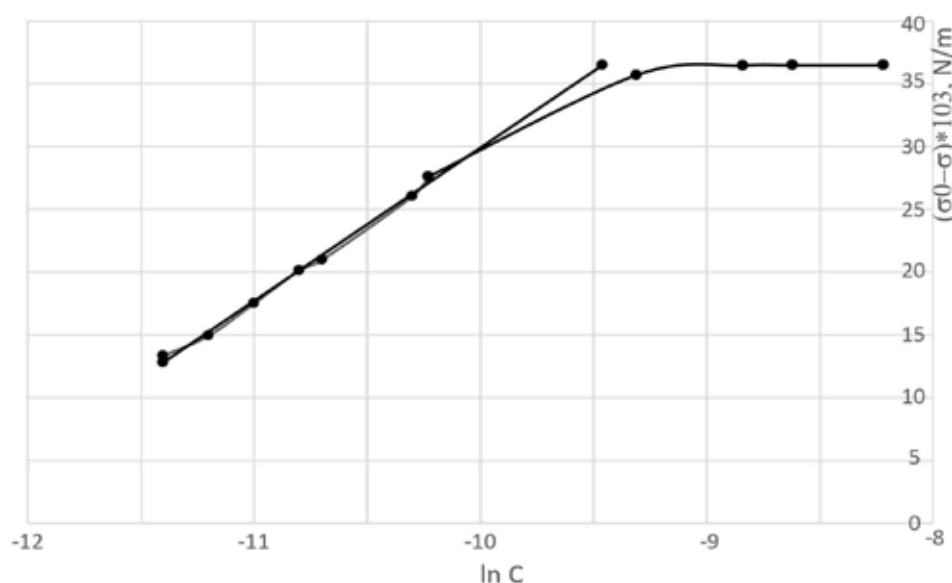


Table 2. Adsorption characteristics of surfactants

Surfactant	Ck, mole fraction	K	S, %	T, K
sodium 4-hexadecyl sulfate	$8,99 \times 10^{-6}$	$1,4 \times 10^7$	99,2	293
sodium dodecyl sulfate	$7,95 \times 10^{-5}$	$2,5 \times 10^5$	95,2	293

4. Practical Significance

It should be noted that the effect of micellization on the rate of formation of the adsorption layer may influence the technological properties of surfactant solutions. For example, in a cleaning process involving disruption of a contaminant layer, not only the reduction in surface tension but also the kinetics of transport of surfactant molecules and aggregates to the interface with the oil phase are important.

From a technological standpoint, not only the equilibrium value of surface tension but also the rate of formation of the surface layer is important. Therefore, surfactant association processes in the bulk solution, which change the concentration of available monomers and the kinetics of their transport to the surface, may potentially affect wetting, emulsification, and the cleaning action of the solutions. Specific kinetic measurements are required for quantitative confirmation of such an effect.

In subsequent studies, the authors intend to present the results of further investigation of the factors affecting the properties of surfactant solutions.

5. Conclusion

The data considered show that, for some of the surfactants studied, the dependence of surface tension on $\ln C$ before C_k is reached is close to linear, while the calculated degree of surface coverage at C_k approaches the limiting value. For ionic surfactants, deviation from linearity may occur even before the CMC and, along with the proposed probabilistic interpretation, may be associated with premicellar association and changes in the activity of monomeric surfactant forms. The Langmuir model and the Szyszkowski equation retain practical value as an approximate calculation framework in the region where the experimental dependence remains linear. A repeated change in surface tension at higher concentrations should be considered cautiously as a possible manifestation of structural reorganization and a change in the growth regime of micellar aggregates associated with the second CMC. The results obtained confirm the need for further joint analysis of the equilibrium and kinetic characteristics of adsorption and micellization.

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Contact: stanislav.derman@gmail.com