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Abstract

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On Micelle Formation in Solutions of Surface-Active Substances

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For natural soaps and synthetic soap-like surface-active substances (SAS), the existence of a critical micelle concentration (C_k) is characteristic; above it these compounds in solutions exist partly in the form of micelles, which are in thermodynamic equilibrium with the molecules or ions forming them ([1]). It was usually assumed that the process of formation of spherical micelles, arising in dilute aqueous solutions, begins and ends within such a narrow concentration interval that it can practically be regarded as a concentration point corresponding to C_k ([2–4]).

On the other hand, in a number of works it was established that for one and the same substance not one, but several values of C_k are found, which was associated with a more complex dependence of the process of association of molecules (ions) on concentration ([5]). In other cases this result was ascribed to the presence of impurities in the preparations studied ([6]) or to peculiarities of the measurement methods used ([7,10]).

Thus, the question of whether the existence, for SAS, of a critical **region** of concentrations, within which the process of micelle formation takes place and two (or more) values of C_k are recorded, can be regarded as real, and what meaning should be attached to these points, remained unresolved.

The formation of micelles is accompanied by a sharp change in the properties of solutions, which is used to determine the value of C_k by measuring turbidity, surface tension, titration with dyes, and other methods ([8–10]).

Among these methods, measurements of surface tension occupy a special place, making it possible to establish a connection between micelle formation in the bulk of the solution and the process of formation of an adsorption layer on its surface, as we showed in joint measurements of the static (σ_s) and dynamic (σ_d) surface tension of SAS solutions ([11]). Below, in Table 1, we give data obtained by us in determining C_k in solutions of anionic, cationic, and nonionic SAS over a sufficiently wide concentration range (C) by various methods. The turbidity of the solutions was measured with a nephelometer (model FEK-N-57) and characterized by values of optical density D; the surface tension was measured by the stalagmometric method with the duration of existence of the

interface $\tau = 2$ min and $\tau = 2$ sec ([12]), and in titration pinacyanol chloride and eosin were used as dyes.*

In Fig. 1 are presented the curves of the dependence $D - \log C$, $\sigma_s - \log C$, and $\sigma_d - \log C$ for solutions of one of the surface-active substances investigated–Na salt of diethylhexyl ether of sulfosuccinic acid

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* N. E. Khokhlova participated in the work.

Table 1

Critical micelle-formation concentrations (for preparations 1-4 in mol/L, for preparation 5 in %)

Surfactants	Nephelometry $(C_k)_1$	Nephelometry $(C_k)_2$	Dye titration $(C_k)_1$	Dye titration $(C_k)_2$	Surface-tension measure-ments $(C_k)_1$	Surface-tension measure-ments $(C_k)_2$
1. Na salt of di-ethyl-hexyl ester of sulfos-uccinic acid (aerosol OT)	0,0025	0,0049	0,0026*	0,0050*	0,0027	0,0052
2. Na salt of di-hexyl ester of sulfos-uccinic acid (aerosol MA)	–	–	0,014*	0,031*	–	–

Figure 1. Dependence of optical density on the concentration of aerosol OT solutions (1). Isotherms of static (2a) and dynamic (2b) surface tension of the same solutions.

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Surfactants	Nephelometry $(C_k)_1$	Nephelometry $(C_k)_2$	Dye titration $(C_k)_1$	Dye titration $(C_k)_2$	Surface-tension measure-ments $(C_k)_1$	Surface-tension measure-ments $(C_k)_2$
3. Na salt of dide-cyl ester of sulfos-uccinic acid	—	—	0,00022*	0,00045*	—	—
4. Do-decy-lamine ac-etate (Amak 1120)	0,0020	0,013	0,0024**	0,012**	0,0030	0,010
5. Prepa-ration DB***	0,025	0,095	0,023*	0,075*	0,026	0,085

* Titration with pinacyanol chloride.
** Titration with eosin.
*** Preparation DB is a polyethylene glycol ether, predominantly of ditertiary butylphenol
$C(CH_3)_3 \cdot C(CH_3)_3 \cdot C_6H_4O(C_2H_4O)_6C_2H_4OH$.

(aerosol OT). As can be seen, on the curve of the dependence $D-\log C$ two break points are found, which plainly indicates the existence of a definite concentration region within which micelle formation occurs in dilute solutions.

Fig. 1. Dependence of optical density on the concentration of aerosol OT

solutions (1). Isotherms of static (2a) and dynamic (2b) surface tension of the same solutions.

The first of these points corresponds to the appearance of micelles in what was previously a molecular or ionic solution and, consequently, is the usual value of C_k [13], which, therefore, should be regarded as the initial concentration limiting the critical region on the left. We regard it as the first value of C_k and denote it by $(C_k)_1$.

The second break point on the curve, corresponding to a sharply expressed maximum, evidently bounds the micelle-formation region on the right and is denoted by us as $(C_k)_2$. It should be emphasized that although the decrease in the turbidity of solutions in the concentration region above $(C_k)_2$ is difficult to explain*, nevertheless it is clear that this quantity, being connected with certain features of the micelle-formation process, has real physical meaning. This follows clearly from the fact that it, like the quantity $(C_k)_1$, is determined not only nephelometrically but also by all the other methods.

* A maximum on the curve of the dependence of the turbidity of solutions on concentration was also found for the nonionic compound Triton X-100 [14].

Indeed, it follows from Fig. 1 that, for aerosol-OT solutions, there is a strict quantitative correspondence between the positions of the points $(C_k)_1$ and $(C_k)_2$, determined from curve 1 of the dependence D—$\log C$, and the points of inflection on the surface-tension isotherms measured, respectively, under static (curve 2a) and dynamic (curve 2b) conditions. The mean values for these points are 0.0026 and 0.0050 mole/liter.

It is also important to note that the equilibrium, lowest values $\sigma_{s\,\min}$ and $\sigma_{d\,\min}$ on both curves 2a and 2b coincide; this means that, at solution concentrations $C > (C_k)_2$, the rate of decrease of the surface tension and, consequently, the rate of formation of the adsorption layer become practically independent of the duration of existence of the interface [11]*.

As can be seen from Table 1, analogous results were also obtained with the other compounds studied—in all cases, irrespective of the chemical composition and molecular structure of the surfactant, as well as of the presence of foreign impurities, two values of C_k were found, with good agreement between the measurement data obtained by different methods. The fact that the second critical point is recorded on the nonequilibrium isotherm of dynamic surface tension σ_s—$\log C$ as the point of its intersection with the static (equilibrium) isotherm σ_s—$\log C$ makes it possible, in interpreting the course of the micelle-formation process in aerosol-OT solutions in the concentration region bounded by $(C_k)_1$ and $(C_k)_2$, to proceed from kinetic concepts.

In the initial concentration region $0 < C < (C_k)_1$, as C increases, an adsorption layer is formed, and the surfactant is present in the bulk of the solution in the molecular (ionic) state. At $C = (C_k)_1$, saturation of the layer is reached (adsorption $\Gamma \to \Gamma_m$) and, correspondingly, the greatest decrease in the static

surface tension ($\sigma_s = \sigma_{\min}$), after which, with a further increase in C, the excess number of molecules (ions) in the bulk of the solution associates into micelles. This process corresponds to the sharp rise of the curve D—$\log C$ up to the greatest value D_m at $C = (C_k)_2$, when the increase in the number of micelles ceases.

Thus, $(C_k)_1$ simultaneously records two coupled changes in the molecular state, respectively, of the bulk of the solution (the appearance of micelles) and of its surface layer (cessation of adsorption-layer formation). At the same time, under dynamic (kinetic) conditions at $\tau = 2$ sec, which are easily realized experimentally, saturation of the layer occurs not at $(C_k)_1$, but at $(C_k)_2$, when σ_d also assumes its smallest value, coinciding with the corresponding value $\sigma_{s\,\min}$**. On the other hand (see Fig. 1), as $C \to (C_k)_2$, not only does micelle formation end, but the adsorption rate, increasing rapidly, becomes (at the point of intersection of the isotherms σ_s—$\log C$ and σ_d—$\log C$) practically independent of τ.

Obviously, it may be assumed that the decrease in the rate of establishment of adsorption equilibrium in the critical region $(C_k)_1 < C < (C_k)_2$

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* It should be pointed out that, on the isotherm σ_s—$\log C$, the lowest values of σ_s correspond to equilibrium values characteristic of each measurement method, but not to static values, which can be obtained, as we have established, only by means of truly static methods–for example, the suspended-drop method [12]. This is evidently due to the fact that, when semistatic methods are used (for example, stalagmometric methods, or methods based on the greatest pressure of bubble formation), the interface surface (drop, bubble), in the process of its formation even with a long lifetime ($\tau \to \infty$), is deformed, which prevents the attainment of static surface-tension values.

** The values of $\sigma_{s\,\min}$ in the region $C > (C_k)_1$ remain practically constant, which distinguishes the course of the surface-tension isotherms of micelle-forming substances from that of soap-like surfactants (organic acids, alcohols, etc.). The reason for this is that, beginning with $(C_k)_1$, all surfactant molecules (ions) autosolubilize.

(cf. curves 2a and 2b) is associated with the slow rate of formation and destruction of micelles in the bulk of the solution (see, for example, [15]), which shifts to the right the equilibrium of the "adsorption desorption" process. When, however, the concentration is increased to the value $C = (C_k)_2$, the dynamic equilibrium between these two processes, occurring respectively in the bulk and in the surface layer, is established at a very high rate. Despite the complexity of a more detailed theoretical analysis of the question under consideration, the totality of the data obtained confirms that the processes of micelle formation and adsorption, expressing one and the same tendency of solutions of long-chain soap-like surfactants to lower the free surface energy at the water/air or water/hydrocarbon-chain interface, are directly connected with one another.

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CITED LITERATURE

[1] J. W. McBain, *Colloid Science*, Boston, 1942, p. 240; D. G. Davies, C. R. Bury, J. Chem. Soc., 1930, 2263.
[2] A. E. Alexander, P. Johnson, *Colloid Science*, 2, Oxford, 1949, p. 667.
[3] G. S. Hartley, J. Chem. Soc., 1938, 1968.
[4] P. A. Rehbinder, K. A. Pospelova, Acta phys.-chim., 16, 71 (1942).
[5] P. Ekwall, Koll. Zs., 136, 37 (1954).
[6] E. F. Williams, N. T. Woodberry, J. K. Dixon, J. Coll. Sci., 12, No. 5, 454 (1957).
[7] M. L. Miller, J. K. Dixon, J. Coll. Sci., 13, No. 5, 411 (1958).
[8] A. Schwartz, D. Perry, *Surface-Active Agents*, IL, 1953.
[9] M. L. Corrin, W. D. Harkins, J. Am. Chem. Soc., 69, 679 (1947).
[10] A. B. Taubman, V. V. Konstantinova, A. S. Kryukova, *Chemistry and Technology of Fuels and Oils*, No. 3, 61 (1960).
[11] S. A. Nikitina, A. B. Taubman, DAN, 116, No. 1, 113 (1957).
[12] S. A. Nikitina, Dissertation, Moscow, 1957.
[13] P. Debye, Ann. N. Y. Acad. Sci., 51, art. 4 (1949).
[14] T. M. Doscher, G. E. Myers, D. C. Atkins, J. Coll. Sci., 6, 223 (1951).
[15] T. Nash, J. Coll. Sci., 14, 59 (1959).

Note: Figure translations are in progress. See original paper for figures.