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CRITICAL MICELLAR CONCENTRATION OF SURFACTANT SOLUTIONS WHEN ADDITIVES WITH DIFFERENT SOLUBILITIES ARE PRESENT IN THE SOLVENT

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Abstract. The aim of the present work is the theoretical investigation of the influence of dissolved additives with small enough and finite concentrations upon the critical micellar concentrations (CMC) of surfactants. According to the theory developed by us, for each surfactant the addition of an additive leads to a decrease of CMC as compared with CMC without an additive. A maximal value of the concentration of the additive upon which the CMC could not be defined any more has been shown to exist.

Резюме. Целью настоящей работы является теоретическое исследование влияния растворенных примесей с достаточно низкой или с крайней концентрацией на величину критической концентрации мицелообразования (ККМ) поверхностно-активных веществ. Согласно развитой нами теории, для каждого поверхностно-активного вещества добавление примеси ведет к уменьшению ККМ по сравнению с ККМ без примесей. Показано, что существует максимальное значение концентрации примеси, выше которого ККМ не может быть более определено.

Introduction

It is well known that the solubilization of hydrophobic molecules in water increases considerably when surfactants are present in the solution. It is due to the fact, that above a certain concentration (CMC) the molecules of surfactant aggregate in micelles. The hydrophobic cores of these micelles are the place, where hydrophobic molecules can be situated, i. e. solubilized.

In the present paper the process of solubilization is intensively investigated because of its importance both in science and industry [1]. Our aim in this work is to establish how the additive molecules influence CMC of the surfactant. This should provide us a tool to study the interactions among the molecules of the solvent, the detergent and the additive.

Experimental data exists, which indicate that the additive in the system water — surfactant can increase, decrease or can not change the CMC. The relation between the concentration of the additives and CMC has been investigated both for ionic [2—8], and nonionic [5,9—16,29] detergents (the literature on this problem is very rich and we do not pretend to review entirely it). In most of the cases the additives decrease CMC, at least when their concentrations are low enough. For the aliphatic alcohols a linear relationship between the ability of the substance to decrease CMC and the number of carbon atoms in the aliphatic chain is obtained [3,4]. But there is data too, indicating that some additives increase CMC at low concentrations. For example the addition of the aromatic alcohols alcylbensyldimethylammonium chlorides [2], glycerol to sodium dodecylsulphate [5], and ethanol to nonionic (9—16) or ionic [17] detergents leads to such results.

In contrast to the experimental investigations, the theoretical considerations on solubilization are less numerous. In some of them it is accepted that the micelles of the detergent are monodispersed and form a monophase in which the additive molecules [18] solubilizate. In general, these molecules can belong to another surface-active substance which is also able to form micelles [19]. Usually in theories like this the fact that the mean number of molecules per micelle as well as the chemical potential of the detergent molecules change in the process of solubilization is not taken into account. In some other theories the polydispersity of the molecules is also considered [20—23]. Similar theoretical considerations were used earlier for an explanation of the micelle formation [24—27]. For the explanation of the polydispersity it is necessary an account of the dependence of the chemical potential of the mixed micelle on the number of the constituting molecules to be rendered.

Theory

Let us consider a system which consists of a solvent, a surfactant with a concentration not much different from the CMC, and an additive with a low concentration. For the description of the ternary system: solvent — surfactant — additive, we use the theoretical approach of Nagarajan and Ruckenstein [21], and a generalization of the proposed by Israelachvili et al. [28] definition for CMC. All extensive quantities of the system will be referred to one molecule of the solvent (i. e. their molar concentrations will be considered in reference to the solvent). We denote with q_{ij} the concentration of micelles, consisting of i molecules of the detergent and j molecules of the additive. Let t and s be the monomer concentrations of the detergent and the additive respectively; let n and m be the total concentrations of the detergent and the additive respectively. Then, accorging to Nagarajan and Ruckenstein [21],

$$q_{ij}=(t)^i(s)^j\alpha_{ij}, \text{ where } \alpha_{ij}=\exp\left(-\frac{\mu_{ij}-i\mu^{\text{det},s}-j\mu^{\text{ad},s}}{kT}\right). \tag{1}$$

In formula (1) μ_{ij}, $\mu^{\text{det},s}$ and $\mu^{\text{ad},s}$ are the standard chemical potentials of the micelle containing i surfactant and j additive molecules, of the monomers of the detergent in the solution, and of the monomers of the additive in the solution respectively, k is the Boltzmann constant and T is the absolute temperature. The total concentration n of the surfactant can be expressed as

$$n=t+\sum_{i=2}^{\infty} iq_{i0}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} iq_{ij}=t+\sum_{i=2}^{\infty} i(t)^i\alpha_{i0}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i(t)^i(s)^j\alpha_{ij}. \tag{2}$$

We generalize the definition for CMC, given by Israelachvili et al. [28], referring to two component systems, as follows: CMC is half of the total concentration of the detergent, for which the number of the surfactant monomers is equal to the number of the surfactant molecules in all the aggregates, i. e. if $n=2t$, then CMC$=n/2=t$. The aggregate comprises at least two molecules of the surfactant and/or the additive.

Let for a given m, n is chosen to be $n=2t$. Then from (2) it follows that this equality is fulfilled:

$$\mathrm{CMC}=t=\sum_{i=2}^{\infty} i\,(t)^i\alpha_{i0}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i\,(t)^i\,(s)^j\alpha_{ij}, \tag{3}$$

where t is a function of s: $t=t(s)$. We denote with $t_0=t(0)=\mathrm{CMC}_0$ — the critical micellar concentration of the surfactant without additives. t_0 can be determined by the implicit equation

$$t_0=\sum_{i=2}^{\infty} i\,(t_0)^i\alpha_{i0}. \tag{3a}$$

The total concentration m of the additive is:

$$m=s+\sum_{j=2}^{\infty} jq_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} jq_{ij}=s+\sum_{j=2}^{\infty} j\,(s)^j\alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j\,(t)^i\,(s)^j\alpha_{ij}. \tag{4}$$

It is clear that $m=m(s)=m[s,\ t(s)]$. From (4) it follows that $m(0)=0$. From (3) and (4), $\mathrm{CMC}=t$ and s can be determined as implicit functions of m. The differentiation of (3) with respect to s gives:

$$\frac{\partial t}{\partial s}=\frac{\partial t}{\partial s}\sum_{i=2}^{\infty}(i)^2\,(t)^{i-1}\alpha_{i0}+\frac{\partial t}{\partial s}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(i)^2\,(t)^{i-1}\,(s)^j\alpha_{ij}$$
$$+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij\,(t)^i\,(s)^{j-1}\alpha_{ij}. \tag{5}$$

Taking into account that

$$\frac{\partial t}{\partial s}=\frac{\partial t}{\partial m}\,\frac{\partial m}{\partial s}, \tag{6}$$

from (5) and (6) it follows:

$$\frac{\partial t}{\partial m}\left(1-\sum_{i=2}^{\infty}(i)^2\,(t)^{i-1}\alpha_{i0}-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(i)^2\,(t)^{i-1}\,(s)^j\alpha_{ij}\right)$$
$$=\frac{1}{(\partial m/\partial s)}\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij\,(t)^i\,(s)^{j-1}\,\alpha_{ij}\right). \tag{7}$$

After the differentiation of (4) with respect fo s, for $\partial m/\partial s$ we obtain the following expression:

$$\frac{\partial m}{\partial s}=1+\sum_{j=2}^{\infty}(j)^2(s)^{j-1}\alpha_{0j}+\frac{\partial t}{\partial s}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij\,(t)^{i-1}\,(s)^j\alpha_{ij}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(j)^2\,(t)^i\,(s)^{j-1}\alpha_{ij}. \tag{8}$$

Substituting (6) in (8), we obtain for $\partial m/\partial s$

$$\frac{\partial m}{\partial s}=\frac{1+\sum_{j=2}^{\infty}(j)^2(s)^{j-1}\alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty}(j)^2(t)^j(s)^{j-1}\alpha_{ij}}{1-\frac{\partial t}{\partial m}\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij(t)^{i-1}(s)^j\alpha_{ij}\right)}. \tag{9}$$

Let us substitute (9) in (7). When we solve the obtained expression with respect to $\partial t/\partial m$, the result is:

$$\frac{\partial t}{\partial m}=\frac{\partial \mathrm{CMC}(m)}{\partial m}=\frac{P(t,\, s)}{Q(t,\, s)}, \tag{10}$$

where

$$P(t,\, s)=\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij\,(t)^i\,(s)^{j-1}\alpha_{ij} \tag{11}$$

$$Q(t,\, s)=\left\{\left(1-\sum_{i=2}^{\infty} i^2\,(t)^{i-1}\alpha_{i0}-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i^2\,(t)^{i-1}\,(s)^j\alpha_{ij}\right)\right.$$
$$\times\left(1+\sum_{j=2}^{\infty} j^2\,(s)^{j-1}\alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j^2\,(t)^i\,(s)^{j-1}\alpha_{ij}\right)$$
$$\left.+ts\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij\,(t)^{i-1}\,(s)^{j-1}\alpha_{ij}\right)^2\right\}. \tag{12}$$

First we shall consider the case, when the concentration of the additive is small enough; then the behavior in the system can be described with the derivative $\left.\frac{\partial \mathrm{CMC}\,(m)}{\partial m}\right|_{m=0}$ $\approx\frac{\mathrm{CMC}\,(m)-\mathrm{CMC}\,(0)}{m}$, where CMC($m$) is the dependence of the CMC on the total concentration m of the additive. Taking in (10) the limit $s\rightarrow 0$ (which is equivalent to $m\rightarrow 0$) and using that $t(0)=t_0$, we obtain for this derivative the following result:

$$\left.\frac{\partial \mathrm{CMC}\,(m)}{\partial m}\right|_{m=0}=\left.\frac{\partial t\,(m)}{\partial m}\right|_{m=0}=\frac{\sum_{i=1}^{\infty} i\,(t_0)^i\alpha_{i1}}{\left(1-\sum_{i=2}^{\infty} i^2\,(t_0)^{i-1}\alpha_{i0}\right)\left(1+\sum_{i=1}^{\infty}(t_0)^i\alpha_{i1}\right)}. \tag{13}$$

Formula (13) presents one of the important results of the theory: the sign of the derivative depends only on the first expression of the denominator in the right-hand side of (13); all other terms in (13) are positive. This expression does not depend on the nature of the additive. We shall prove that

$$\left(1-\sum_{i=2}^{\infty} i^2\,(t_0)^{i-1}\,\alpha_{i0}\right) \text{ is negative.}$$

From (3a), after dividing by t_0, we obtain

$$1=\sum_{i=2}^{\infty} i\,(t_0)^{i-1}\alpha_{i0}. \tag{14}$$

It is clear, that

$$\sum_{i=2}^{\infty} i\,(t_0)^{i-1}\alpha_{i0}<\sum_{i=2}^{\infty} i^2\,(t_0)^{i-1}\alpha_{i0}. \tag{15}$$

From (14) and (15), it follows that

$$1-\sum_{i=2}^{\infty} i^2\,(t_0)^{i-1}\alpha_{i0}<0. \tag{16}$$

And namely because this expression determines the sign of the derivative $\left.\frac{\partial \mathrm{CMC}(m)}{\partial m}\right|_{m=0}$ we conclude that this derivative is always negative, i. e. $\left.\frac{\partial \mathrm{CMC}(m)}{\partial m}\right|_{m=0} < 0$. Consequently, for low enough concentrations of the additive, CMC must be lower than the CMC in the absence of additives.

Furthermore we investigate the dependence of CMC on the concentration of the additive with finite concentrations. We consider the case when the concentrations of the surfactant and the additive, although finite should be low enough so that in the system a phase transition should not take place.

The numerator $P(t, s)$ on the right-hand side of (10) is a quantity, which is always positive, when $t>0$. This means, that if we consider m as a function of t, $m=f(t)$, then this function is a simple function of t. But CMC (0) also has just one definite value because it can be proved easily that the solution of eq. (3) when $s=0$, is the only one possible. We have proved that $\left.\frac{\partial \mathrm{CMC}(m)}{\partial m}\right|_{m\to 0}<0$; consequently a value of CMC(m) does not exist for $m>0$, such that CMC(m) to be bigger than CMC(0). The denominator $Q(t, s)$ in the right-hand side of the expression (9) is well defined for each value of t and s, consequently it cannot reach the value $\pm\infty$. There is a possibility for the existence of some finite concentrations m' of the additive for which $Q(t, s)$ becomes equal to zero. In this case the derivative of CMC with respect to m can change its sign at $m=m'$. Further on we investigate the cases when m' exists. A necessary condition for the existence of m' is the following system to have a solution with respect to t, s and m:

$$\left|\begin{array}{l} t=\sum_{i=2}^{\infty} i(t)^i \alpha_{i0}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i(t)^i(s)^j \alpha_{ij} \\ m=s+\sum_{j=2}^{\infty} j(s)^j \alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j(t)^i(s)^j \alpha_{ij} \\ Q(t, s)=0. \end{array}\right. \tag{17}$$

In (17), $Q(t, s)$ is given by (12). One solution of this system is

$$s=s_0, \quad m=m_0, \tag{18}$$

and

$$t=0, \tag{19}$$

where s_0 is a solution of the equation

$$\sum_{j=1}^{\infty} (s_0)^j \alpha_{1j}=1 \tag{20}$$

and m_0 is expressed by s_0 as

$$m_0=s_0+\sum_{j=2}^{\infty} j(s_0)^j \alpha_{0j}. \tag{21}$$

Let us suppose that there is another solution t_1, s_1, m_1 of this system with $s_1 \neq s_0$ (when $s_1=s_0$, it is easy to be shown that $t_1=0$ and $m_1=m_0$). First we shall prove that s_1 cannot be greater than s_0. Let us suppose that $s_1>s_0$. Then the first equation of (17) can be satisfied only for $t_1=0$. For $t_1>0$ the first derivative with respect to t_1 of the expression on the right-hand side of the first equation of (17) is greater than 1, while the same derivative for the expression on the left-hand side of the same equation is strictly equal to 1. The two expressions are equal when $t_1=0$. Consequently they cannot be equal for $t_1>0$. But if $t_1=0$ and $s_1>s_0$, the inequality $Q(t_1, s_1)\neq 0$ is fulfilled. In this way we conclude that a solution of the system (17) with $s_1>s_0$ cannot exist. If s_1 exists, it must be less than s_0. For such s_1, its corresponding t_1 is bigger than zero (in the contrary case the equation $Q(t_1, s_1)=0$ cannot be satisfied). For $t_1>0$ and $s_1<s_0$, $m_1(t_1, s_1)\neq m_0$ can exist. In this case a question arises about the value of m_1 with respect to m_0. We showed that $m=f(\text{CMC})$ is well defined in the interval [0, CMC(0)], as $m[\text{CMC}(0)]=0$ and $m(0)=m_0$. We showed also, that a necessary condition for existence of solution m_1, t_1, s_1 of the system (17), so that $(m_1, t_1, s_1)\neq(m_0, 0, s_0)$, is $s_1<s_0$. But it can be shown, that cases exist, when $m_1>m_0$, although $s_1<s_0$. We will seek for a sufficient condition for the existence of such possibilities.

From (10), (11), (12) and (20) it can be seen, that the numerator and the denominator in the expression (10) are equal to zero when $t=0$, $s=s_0$ and $m=m_0$. To find its value at $m=m_0$, we present $P(t, s)$ from (11) and $Q(t, s)$ from (12) in the following way:

$$P(t, s)=t\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij(t)^{i-1}(s)^{j-1}\alpha_{ij}\right) \tag{22}$$

$$Q(t, s)=t\left\{\left(\frac{1-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i^2(t)^{i-1}(s)^j\alpha_{ij}}{t}-\frac{\sum_{i=2}^{\infty} i^2(t)^{i-1}\alpha_{i0}}{t}\right)\right. \tag{23}$$

$$\times\left(1+\sum_{j=2}^{\infty} j^2(s)^{j-1}\alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j^2(t)^i(s)^{j-1}\alpha_{ij}\right)$$

$$\left.+s\left(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij(t)^{i-1}(s)^{j-1}\alpha_{ij}\right)^2\right\}.$$

Then

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}}\frac{\partial\text{CMC}(m)}{\partial m}=\frac{M(t, s_0)}{N(t, s_0)} \tag{24}$$

$$M(t, s_0)=\sum_{j=1}^{\infty} j(s_0)^{j-1}\alpha_{1j} \tag{25}$$

$$N(t, s_0)=\left\{\left(\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}}\frac{1-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i^2(t)^{i-1}(s)^j\alpha_{ij}}{t}-4\alpha_{20}\right)\right. \tag{26}$$

$$\left.\times\left(1+\sum_{j=2}^{\infty} j^2(s_0)^j\alpha_{0j}\right)+s_0\left(\sum_{j=1}^{\infty} j(s_0)^{j-1}\alpha_{1j}\right)^2\right\}.$$

But

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{1-\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i^2 (t)^{i-1}(s)^i \alpha_{ij}}{t} = \lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{1-\sum_{j=1}^{\infty}(s)^j\alpha_{1j}}{t} - 4\sum_{j=1}^{\infty}(s_0)^j\alpha_{2j}. \tag{27}$$

After applying the l'Hospital theorem we obtain:

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{1-\sum_{j=1}^{\infty}(s)^j\alpha_{ij}}{t} = \frac{-\lim\limits_{t\to 0}\frac{\partial s}{\partial m}\sum_{j=1}^{\infty} j(s_0)^{j-1}\alpha_{1j}}{\lim\limits_{t\to 0}\frac{\partial t}{\partial m}}. \tag{28}$$

We denote

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{\partial t}{\partial m} = \lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{\partial \mathrm{CMC}(m)}{\partial m} = X. \tag{29}$$

Then (28) can be presented as follows:

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{1-\sum_{j=1}^{\infty}(s)^j\alpha_{1j}}{t} = \frac{-\lim\limits_{t\to 0}\frac{\partial s}{\partial m}\sum_{j=1}^{\infty} j(s_0)^{j-1}\alpha_{1j}}{X}. \tag{30}$$

To find $\lim\limits_{t\to 0}\frac{\partial s}{\partial m}$ we use that $\frac{\partial s}{\partial m}=\left(\frac{\partial m}{\partial s}\right)^{-1}$, where $\frac{\partial m}{\partial s}$ is given by (9):

$$\frac{\partial s}{\partial m} = \frac{1-\frac{\partial t}{\partial m}\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij(t)^{i-1}(s)^j\alpha_{ij}}{1+\sum_{j=2}^{\infty} j^2(s)^{j-1}\alpha_{0j}+\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j^2(t)^i(s)^{j-1}\alpha_{ij}} \tag{31}$$

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{\partial s}{\partial m} = \frac{1-X\sum_{j=1}^{\infty} j(s_0)^j\alpha_{1j}}{1+\sum_{j=2}^{\infty} j^2(s_0)^{j-1}\alpha_{0j}}. \tag{32}$$

The result of the substitution of (32) in (30) is

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{1-\sum_{j=1}^{\infty}(s)^j\alpha_{1j}}{t} = \frac{-\left(1-X\sum_{j=1}^{\infty} j(s_0)^j\alpha_{1j}\right)\cdot\sum_{j=1}^{\infty} j(s_0)^{j-1}\alpha_{1j}}{X\left(1+\sum_{j=2}^{\infty} j^2(s_0)^{j-1}\alpha_{0j}\right)}. \tag{33}$$

From (33), (27) and (24)

$$\lim_{\substack{t\to 0\\ \binom{m\to m_0}{s\to s_0}}} \frac{\partial \mathrm{CMC}(m)}{\partial m}=\frac{\sum\limits_{j=1}^{\infty} j\,(s_0)^j \alpha_{1j}}{\left(\sum\limits_{j=1}^{\infty} j\,(s_0)^j \alpha_{1j}\right)^2-2\left(\sum\limits_{j=0}^{\infty} (s_0)^j \alpha_{2j}\right)\left(s_0+\sum\limits_{j=2}^{\infty} j^2 (s_0)^j \alpha_{0j}\right)}. \tag{34}$$

The numerator of this expression is always positive, but the denominator can be positive, negative, or equal to zero. If the denominator is positive it means that there are cases when this derivative is positive. From the positive sign of the derivative and from the fact that m(CMC) is a simple function of CMC in the interval (0, CMC(0)), it follows that $m_1>m_0$. For this case the dependence of CMC on m is shown qualitatively in Fig. 1*b*. Figure 1*a* presents the case when CMC is a monotonous function of m.

In the ternary phase diagram (solvent — detergent — additive), the boundary between the region of monomeric and predominantly aggregated state can be considered as a limit of the microemulsion region to the side of the high enough solvent concentration. This limit is qualitatively presented in Fig. 2.

In this work we enlarge and correct the results, which are obtained in the previous work [30], where the idea that CMC(m) is defined only for $m<m_0$ was held.

Finally we would like to discuss qualitatively the conditions when s_0 exists and when the situations presented in Figs 1 and 2 are valid. Obviously, s_0 from (20) must

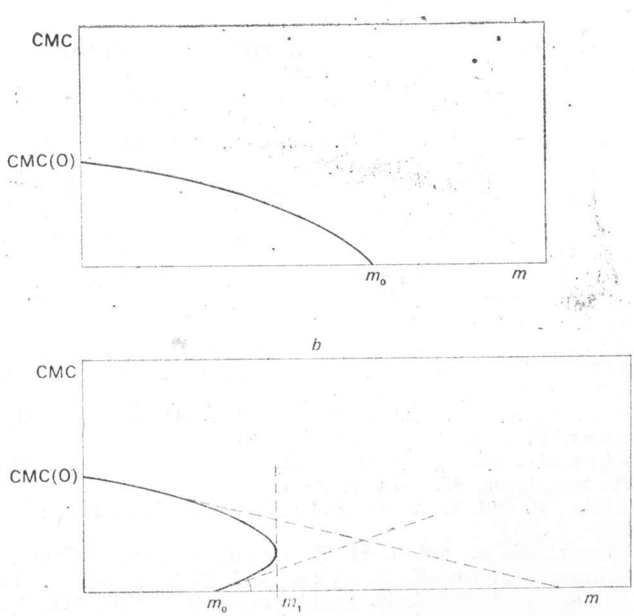

Fig. 1. Dependence of the critical micellar concentration (CMC) on the total concentration m of the additive:
a) when CMC(m) is simple function of m;
b) when $\left.\frac{\partial \mathrm{CMC}(m)}{\partial m}\right|_{m=m_0} \geq 0$

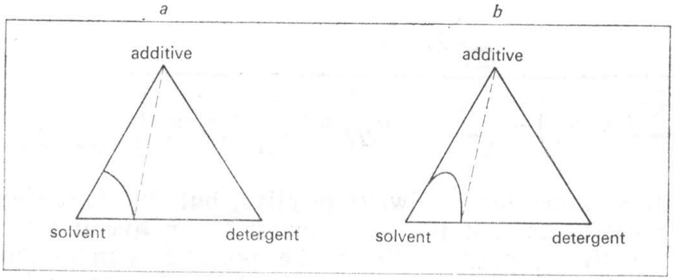

Fig. 2. Limits of the monomeric region in the ternary system solvent — detergent — additive in the cases when:
a) CMC(*m*) is a simple function of *m*;
b) CMC(*m*) is not a simple function of *m*. We note, that this is phase diagram only in case there were no other phase transition

satisfy the inequality $s_0<1$. This is possible if the surfactant and the additive are easily soluble in order to assure that α_{ij} are high enough. The derivative in (34) is positive if the additive is well soluble in the solvent, i. e. there is no tendency for its molecules to aggregate. In this case the situation in Figs 1*b* and 2*b* is expected. In the opposite case of additive that is not well dissolved in the solvent and easily forms aggregates in the solution, the behaviour is presented in Figs 1*a* and 2*a*.

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