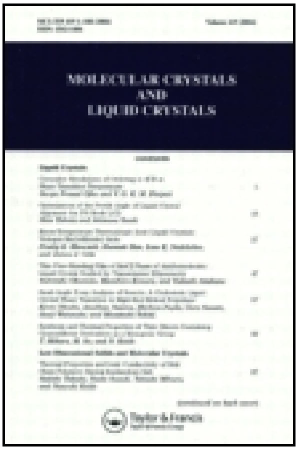

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DEPENDENCE OF THE CRITICAL MICELLAR CONCENTRATION OF SURFACTANTS ON DISSOLVED ADDITIVES WITH FINITE CONCENTRATIONS

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Abstract In an earlier article[1] it was shown that for every surfactant the addition of small enough quantity of additive leads to a decrease of the critical micellar concentration (CMC). The aim of the present work is the determining of the course of the CMC when the additive changes in the range of finite concentrations, which are still low enough to avoid the phase separation. The result obtained is that the CMC keeps decreasing when the quantity of the additive increases in all this range. A maximum value of the concentration of the additive is shown to exist above which the CMC could not be defined any more.

INTRODUCTION

As in our previous work[1] we use for the description of the ternary system solvent - surfactant - additive the theoretical approach of Nagarajan and Ruckenstein[2], and a generalization of the proposed by Israelachvili et al[3] definition for CMC. We consider the case when the concentrations of the surfactant and of the additive are low enough, so that phase transitions do not take place. In the language of the phase diagrams this means that in the triangular phase diagram solvent - surfactant - additive the boundaries of the phase at the vertex of the solvent are not crossed. All the extensive quantities of the system will be referred to one molecule of the solvent (i.e. their molar concentrations with respect to the solvent will be considered).

We denote with q_{ij} the concentration of micelles having i molecules of the detergent and j molecules of the additive. (This implies that some kind of definition of micelle is used.) 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, according to Nagarajan and Ruckenstein[2]:

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

In (1) μ_{ij}, $\mu^{det,s}$, and $\mu^{ad,s}$ 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:

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

We generalize the definition for CMC given by Israelachvili et al[3] 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. An aggregate comprises at least two molecules of the surfactant and/or the additive.

If for a given m, n is chosen so that n=2t, from (2) it follows that this equality is fulfilled:

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

The total concentration m of the additive is:

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

From (3) and (4), CMC=t and s can be expressed as implicit functions of m. We have shown[1] that:

$$\left.\frac{\partial CMC(m)}{\partial m}\right|_{m=0} < 0 \tag{5}$$

Later on in this paper we consider the case of finite concentrations of the additive.

DEPENDENCE OF CMC ON ADDITIVES WITH FINITE CONCENTRATIONS

The dependence of the quantity $\partial CMC(m)/\partial m$ on m can be presented in the following way:

$$\frac{\partial CMC(m)}{\partial m} = \frac{P(t,s)}{Q(t,s)} \tag{6}$$

where

$$Q(t,s) = \{(1 - \sum_{i=2}^{\infty} i^{2}(t)^{i-1}\alpha_{i0} - \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i^{2}(t)^{i-1}(s)^{j}\alpha_{ij})\times$$
$$(1 + \sum_{j=2}^{\infty} j^{2}(s)^{j-1}\alpha_{0j} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j^{2}(t)^{i}(s)^{j-1}\alpha_{ij}) +$$
$$+ ts(\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} (t)^{i-1}(s)^{j-1}\alpha_{ij})^{2}\} \tag{6a}$$

$$P(t,s)=\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} ij(t)^{i}(s)^{j-1}\alpha_{ij} \tag{6b}$$

The numerator at the right-hand-side of (6) is a quantity which is always positive when t>0. The denominator of the same expression is well defined for each value of t and s, consequently it cannot reach the values ±∞. A possibility exists that for some finite concentrations m' of the additive, the denominator becomes equal to zero. In that case the derivative of CMC with respect to m could change its sign at m=m'. Later on we investigate the cases when m' exists. One necessary condition for the existence of m' is that the following system have solution with respect to t, s and m:

$$\left|\begin{array}{l} t = \sum_{i=2}^{\infty} i(t)^{i}\alpha_{i0} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} i(t)^{i}(s)^{j}\alpha_{ij} \\ m = s + \sum_{j=2}^{\infty} j(s)^{j}\alpha_{0j} + \sum_{i=1}^{\infty}\sum_{j=1}^{\infty} j(t)^{i}(s)^{j}\alpha_{ij} \\ Q(t,s) = 0 \end{array}\right. \tag{7}$$

In (7), Q(t,s) is given by (6a). One solution of this system is:

$$t=t_0,\ s=s_0,\ m=m_0, \tag{8}$$

where

$$t_0=0, \tag{8a}$$

s_0 is a solution of the equation

$$\sum_{j=1}^{\infty} (s_0)^{j}\alpha_{1j} = 1 \tag{8b}$$

and m_0 is expressed via s_0 as:

$$m_0 = s_0 + \sum_{j=2}^{\infty} (s_0)^{j}\alpha_{0j} \tag{8c}$$

It can be shown that in the general case this is the only solution of (7). 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 show that $t_1 = t_0$ and $m_1 = m_0$.) There are two possible cases: $s_1 > s_0$ and $s_1 < s_0$. We consider both of them.

a) $s_1 > s_0$. Then the first equation of (7) 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 (7) 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; and because the two expressions are equal when $t_1 = 0$, 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. So solution of the system (7) with $s_1 > s_0$ cannot exist.

b) $s_1 < s_0$. We consider the s_1 with the minimal value, if there are several s_1 with this property. Then $t_1 > 0$ can be calculated from the first equation of (7). We expand m(t,s) in Tailor's series around (t_1, s_1):

$$m(t,s) = m(t_1,s_1) + A(t_1,s_1)(t-t_1) + B(t_1,s_1)(s-s_1) + \ldots \quad (9)$$

where

$$A(t_1,s_1) = \left.\frac{\partial m}{\partial t}\right|_{\substack{t=t_1\\ s=s_1}} ; \qquad B(t_1,s_1) = \left.\frac{\partial m}{\partial s}\right|_{\substack{t=t_1\\ s=s_1}} \quad (9a)$$

In the general case $A(t_1,s_1) \neq 0$ and $B(t_1,s_1) \neq 0$, otherwise the system

$$\left|\begin{array}{l} t_1 = \sum\limits_{i=2}^{\infty} i(t_1)^i \alpha_{i0} + \sum\limits_{i=1}^{\infty} \sum\limits_{j=1}^{\infty} i(t_1)^i (s_1)^j \alpha_{ij} \\ Q(t_1,s_1) = 0 \\ A(t_1,s_1) = 0 \text{ or } B(t_1,s_1) = 0 \end{array}\right. \quad (10)$$

can have solution only if some conditions are imposed on the quantities α_{ij} (cf.(1)).

We denote with R(t,s) the expression:

$$R(t,s) = \sum_{i=2}^{\infty} i(t)^i \alpha_{i0} + \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} i(t)^i (s)^j \alpha_{ij} - t \qquad (11)$$

This is in fact the first equation of the system (7). After decomposing it in Tailor's series, we obtain:

$$R(t,s) = R(t_1,s_1) + C(t_1,s_1)(t-t_1) + D(t_1,s_1)(s-s_1) +.. \qquad (12)$$

where

$$C(t_1,s_1) = \left.\frac{\partial m}{\partial t}\right|_{\substack{t=t_1\\ s=s_1}} ; \qquad D(t_1,s_1) = \left.\frac{\partial m}{\partial s}\right|_{\substack{t=t_1\\ s=s_1}} \qquad (12a)$$

Note that not only $R(t_1,s_1)=0$ but that $R(t,s)=0$ for each t and s, which are implicit functions of m (see the comment preceding formula (5)). Then for $s<s_1$:

$$t-t_1 = -\frac{D(t_1,s_1)}{C(t_1,s_1)}(s-s_1) \qquad (13)$$

The expressions

$$\frac{D(t_1,s_1)}{C(t_1,s_1)} \quad \text{and} \quad \frac{A(t_1,s_1)D(t_1,s_1)}{C(t_1,s_1)} - B(t_1,s_1) \qquad (14)$$

must be also different from zero, otherwise overdetermined systems analogous to (10) will be obtained. Then the derivative from the left to $m(t_1,s_1)$ is:

$$\left.\frac{\partial CMC}{\partial m}\right|_{m=m(t_1,s_1)} = \frac{\dfrac{D(t_1,s_1)}{C(t_1,s_1)}}{\dfrac{A(t_1,s_1)D(t_1,s_1)}{C(t_1,s_1)} - B(t_1,s_1)} \qquad (15)$$

But this is in contradiction with the fact that $Q(t_1,s_1)=0$

and $\left.\frac{\partial CMC}{\partial m}\right|_{m=m_0} = -\infty$. So solution cannot exist with $s_1<s_0$ too.

Consequently the only solution of (7) is given by (8). This result shows that the CMC is a monotone decreasing function of the total concentration of the additive which reaches the value zero when this concentration equals m_0. For $m=m_0$, the derivative $\partial CMC/\partial m$ is not necessarily equal to ∞, because not only the equality $Q(t_0,s_0)=0$ is fulfilled but the equality $P(t_0,s_0)=0$ is true too. Note that m_0 can be reached if a phase transition does not appear for values of $m<m_0$.

The general course of the dependence of CMC on the concentration of the additive m is given in Fig.1.

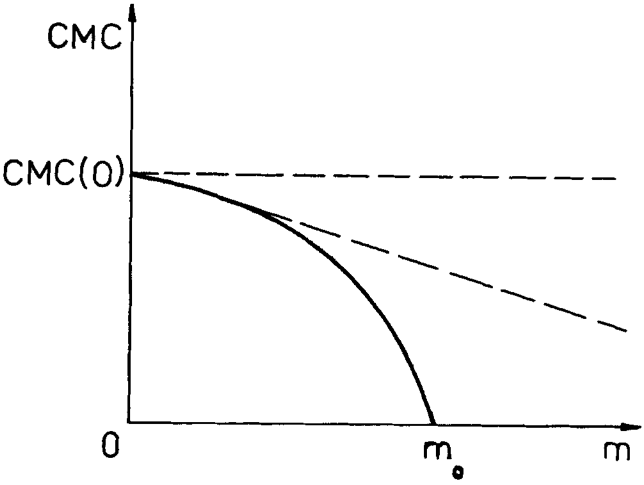

FIGURE 1. General course of the dependence of the critical micellar concentration (CMC) on the quantity of the additive m. The CMC decreases monotonously when m increases. If a phase transition does not take place, the CMC becomes equal to zero at $m=m_0$. (For the definition of m_0 see the text.)

CONCLUSION

In the present work we show that for every surfactant the addition of some quantity of additive even when its concentration is finite, leads to a decrease of the CMC. Most of the experimental studies confirm such a behaviour of the CMC when the concentration of the additive increases. There exist, however, some experimental data which show an inverse tendency of CMC.[4-11] Further on we discuss some possible reasons for this discrepancy.

In the present considerations we use the theory of Nagarajan and Ruckenstein[2] in which it has been supposed that if the micelle has a given number of detergent and additive molecules, its standard chemical potential does not depend on the concentration of the solutes. It is possible that because of the dependence of the time of life of the micelle on this concentration this condition is not fulfilled.

Another reason for the divergence between our theory and the experiments cited above could be our use of a concrete definition for the CMC. The experimental procedures for the precise determination of CMC are always semiempirical. It is necessary that a theory should be developed which connects the experimentally measured quantity with the polydispersity of the micelles for concentrations around the CMC; so CMC consistent with the definitions used will be measured. The corrections introduced in this way may not be negligible.

Finally it can be noted that if the curve CMC(m), with CMC in accordance with our definition, is obtained experimentally, our theory can be used for calculating the quantities α_{ij}.

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