# Behavior of Surfactant Molecules Near the Critical Micelle Concentration: A Statistical Treatment

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**1 AUTHOR:**

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University of Leipzig
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# Behavior of Surfactant Molecules Near the Critical Micelle Concentration: A Statistical Treatment

**Harald Morgner***

*Wilhelm Ostwald-Institute for Physical and Theoretical Chemistry, University Leipzig, Linnéstr. 2, D-04103 Leipzig*

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Several studies report the existence of a local minimum of the surface tension near the critical micelle concentration (CMC) of surfactant solutions. The interpretation of this phenomenon is not unambiguous. While some authors conceive this observation as a normal feature, others consider it to be a clear indication of the presence of an impurity which is more surface active than the surfactant itself. We present a phenomenological description of the behavior of surfactant molecules near the CMC which indicates that a local maximum of the chemical potential can indeed be explained for a pure surfactant solution. This theoretical treatment is applied to the results of an experimental study of the non-ionic surfactant POPC (1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine) dissolved in the polar solvent HPN (3-hydroxypropionitrile) which does not only provide surface tension data but also provides the chemical potential of POPC as a function of the concentration as well. The theory not only provides an explanation for the local maximum of the chemical potential and, thus, for the local minimum of the surface tension, but also gives in addition an estimate of the micelle size.

## Introduction

It is common practice to determine the critical micelle concentration (CMC) of a surfactant solution by means of the surface tension. The CMC is reached when the surface tension does not vary any more with the nominal surfactant concentration in the bulk. In the upper panel of Figure 1, the CMC is to be identified with the concentration $c_1$.

Often, however, the situation is not as easy to interpret. The lower panel of Figure 1 shows a typical situation. The CMC is not unambiguously defined by the experimental data, because the surface tension displays a minimum before leveling off to a constant value. The CMC might then be identified with $c_1$ which is here the concentration where the surface tension passes through the asymptotic value. It might as well be assumed that the minimum of the surface tension at $c_2$ is the CMC. Further, the concentration $c_3$ where the surface tension finally levels off to its asymptotic value can and has been conceived as the true CMC.

Usually, textbooks are reluctant to define a sharp value to the CMC, even though the separation between the three concentrations is not negligible compared with, say $c_2$, but rather point out that the CMC lies somewhere in the range between $c_1$ and $c_3$; see, for example, ref 1.

Some authors would discuss this situation in a very different way. They would not evaluate a CMC from a measured shape as given in Figure 1b. They would claim that this shape is not the signature of a pure solution but a clear indication of the presence of an impurity. This discussion dates back several decades[2,3] and is still going on.[4,5] Very convincing evidence has been presented in this respect. Couper et al.[4] have dissolved 99% pure hexaethylene glycol dodecyl ether (C12E6) in formamide and found a local minimum of the surface tension at a concentration of 0.04 mol/L while a sharp transition to a constant value of the surface tension as in Figure 1a was observed at the quoted concentration after purification. A similar result has been reported by Lin et al.[5] when comparing the surface tension of an aqueous $C_mE_8$ solution with and without a small amount of dodecanol. On the other hand, by studying other systems, the same authors came to the conclusion that the presence or absence of a local minimum in the surface tension cannot be taken as an unambiguous indicator for the presence or absence of impurities.[5]

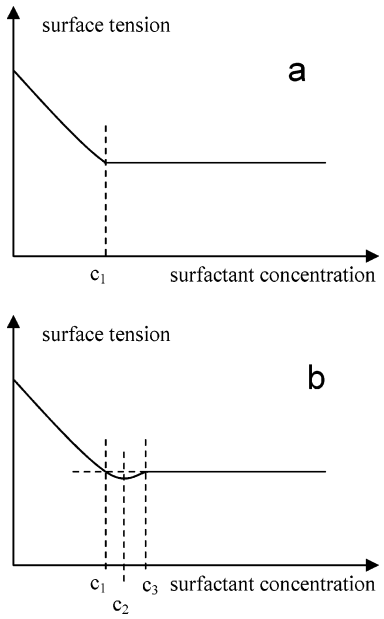


**Figure 1.** Scheme of the surface tension as function of concentration near CMC, (a) ideal shape, (b) commonly observed deviation from ideal shape.

* Corresponding author. E-mail: hmorgner@rz.uni-leipzig.de. Fax: +49-341-97 36090.

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It is obvious that the observed effect of an impurity reflects in the first place the properties of the system investigated and cannot necessarily be generalized. Indeed, in a previous publication from this laboratory, we have reported on a system which does show a local minimum of the surface tension near the critical micelle concentration.[6] The system consisted of a the non-ionic surfactant POPC (1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine) dissolved in the polar solvent HPN (3-hydroxypropionitrile). From two types of measurement, data on surface tension $\sigma$ and direct determination of the surface excess $\Gamma^e$ by NICISS (neutral impact collision ion scattering spectroscopy), it could be effectively argued that no surface active impurity was present, since a possible impurity must be very similar to the surfactant POPC with respect to atomic composition and with respect to its activity coefficient. Thus, the small but significant local minimum of the surface tension exists without the presence of a surface active impurity. From the simultaneous measurement of surface tension and surface excess, the variation of the chemical potential of POPC as a function of the bulk concentration could be evaluated without any model assumption from very low concentration to a concentration well above the CMC via the Gibbs equation

$$d\sigma = -\Gamma^e \cdot d\mu$$

The local minimum of the surface tension leads to a local maximum of the chemical potential.

This finding has motivated the present study. The standard concept of the CMC implies the notion that above the CMC the monomer concentration and, thus, the chemical potential remain constant because any additional surfactant molecules should form micelles. If our observation is correct that close to but above the CMC the chemical potential can exceed its asymtotic value, then this would imply that closely above threshold the formation of micelles is hindered while this hindrance vanishes at higher concentrations.

## Theory: A Statistical Description of the Behavior of Surfactant Molecules Near the Critical Micelle Concentration

**General Remarks.** We will use statistical arguments in order to describe the probability for the formation of micelles. It is obvious that micelle formation is a collective process of a large number of surfactant molecules. Micelle formation will be favored in those regions of the solution where fluctuations lead to a comparatively high local concentration. If one wishes to carry out a calculation, one has to specify two quantities: (1) the probability to find a certain local concentration and (2) a critical local concentration, above which micelles form.

In order to carry through this strategy, we have to define a model which describes the occurrence of density fluctuations. The fact that our experimental study[6] leads to an ideal dissolution behavior of the surfactant below the CMC helps to make use of a simple statistical treatment. The ideal behavior is identical to the statement that below the CMC all surfactant molecules encounter the same situation, irrespective of the actual concentration. This, in turn, indicates clearly that all surfactant molecules below the CMC behave independently of each other. Slightly above the CMC, this behavior is hardly changed. Accordingly, we are justified to consider the positions of surfactant molecules as independent of each other. Thus, for an averaged concentration $C$ of surfactant molecules, given as number of molecules per unit volume, we can assess the probability to find $k$ molecules within a volume $V$ by means of the Poisson distribution

$$P_{\text{Poisson}}(k,V,C) = \frac{(V\cdot C)^k \exp(-V\cdot C)}{k!}$$

We would like to point out, that the applicability of the Poisson distribution should in general be justified better, the lower the bulk concentration is. However, the experimental verification of ideal solution behavior makes the Poisson distribution the perfect choice.

Near the critical micelle concentration, we may assume that micelles are formed in regions with particularly high local concentration. We have no a priori knowledge about how big this local concentration has to be and how many molecules should be within the region.

On the basis of this consideration, we will devise two models. In the first model, we assume the number of surfactant molecules being involved in micelle formation as an unknown but fixed value, and we ask for the maximum volume within which these molecules must be concentrated. In the second model, we assume a fixed, again unknown volume and ask for the minimum number of surfactant molecules within this volume needed for micelle formation. We will find that both models lead to the same answer. In both models, the critical number of surfactant molecules and the critical volume will be determined by comparison to experimental data.

We state at this point that the number of surfactant molecules being involved in micelle formation is not identical to the number of surfactant molecules being part of a micelle. The reason is readily explained. If all surfactant molecules within a certain region would coalesce to form a micelle (the volume of which is orders of magnitude smaller that the volume occupied by the monomers), then around the newly formed micelle a fairly large region void of surfactant molecules would be created. The low chemical potential within this region would be a strong driving force to make the micelle decay immediately. Thus, on the average, only the surplus concentration can form the micelle. This consideration will allow us to give an estimate for the averaged number of surfactant molecules per micelle.

**Model 1.** For a concentration $C$ of surfactant molecules, given as number of molecules per unit volume, we can assess the probability to find $k$ molecules within a volume $V$ by means of the Poisson distribution

$$P_{\text{Poisson}}(k,V,C) = \frac{(V\cdot C)^k \exp(-V\cdot C)}{k!}$$

The Poisson distribution is justified by the typically low concentration that non-ionic surfactant molecules can take on in a solution. For a fixed number $k$ of molecules at known value $C$ for the averaged concentration, the integral over the volume is independent of $k$ and evaluates to

$$\int_0^\infty P_{\text{Poisson}}(k,V,C)\, dV = \frac{1}{C}$$

We define the normalized probability function

$$P(k,V,C) = P_{\text{Poisson}}(k,V,C)\cdot C = \frac{(V\cdot C)^k \exp(-V\cdot C)\cdot C}{k!} \qquad (1)$$

which is normalized with respect to integration over the volume

$$\int_0^\infty P(k,V,C)\, dV = 1$$

For fixed number $k$ of surfactant molecules, the probability allows us to compute the probability to find the local concentration $k/V$.

Near the critical micelle concentration, we may assume that micelles are formed in regions with particularly high local concentration. We define a value $k_{\mathrm{thres}}$ of molecules that must be present to cooperatively lead to the formation of a micelle, and we define a critical volume $V_{\mathrm{thres}}$ such that the $k_{\mathrm{thres}}$ molecules must be concentrated within a volume $V < V_{\mathrm{thres}}$.

The probability for this to happen can then easily be calculated as

$$X_{\mathrm{mic}} = \int_0^{V_{\mathrm{thres}}} P(k_{\mathrm{thres}},V,C)\,\mathrm{d}V \tag{2a}$$

while the probability that $k_{\mathrm{thres}}$ molecules are not sufficiently concentrated to cause formation of a micelle is given as

$$X_{\mathrm{mono}} = \int_{V_{\mathrm{thres}}}^{\infty} P(k_{\mathrm{thres}},V,C)\,\mathrm{d}V \tag{2b}$$

The two quantities add to unity. They can be considered as molar fraction $X_{\mathrm{mic}}$ of surfactant molecules being involved in micelle formation (which is not the same as being part of a micelle) and as molar fraction $X_{\mathrm{mono}}$ of surfactant molecules that are definitely in the state of monomers.

Now, we consider the chemical potential of the surfactant molecules as function of concentration $C$. We assume that the contribution of monomer surfactant molecules to the chemical potential differs from the contribution of those surfactant molecules that are involved in micelle formation. The latter shall have the chemical potential $\mu_{\mathrm{mic}}$ while the monomers have a chemical potential $\mu_{\mathrm{mono}}(C)$ which depends on the concentration $C$. The chemical potential of the surfactant in the entire system is then given as weighted average

$$\mu(C) = X_{\mathrm{mono}}(C)\mu_{\mathrm{mono}}(C) + X_{\mathrm{mic}}(C)\mu_{\mathrm{mic}} \tag{3}$$

The molecules which are not involved in micelle formation are in an environment with a concentration smaller than the averaged concentration $C$ since the regions involved in micelle formation have systematically a relatively high concentration. Thus, the chemical potential for these remaining molecules must be calculated as average over all regions which do not contribute to micelle formation. As the chemical potential is defined only for macroscopic and homogeneous systems, we have to define a value of the local chemical potential $\mu_{\mathrm{local}}(k,V)$ which depends on the number of $k$ of molecules and the volume $V$ within which they are found.

The definition of a local chemical potential is necessarily an arbitrary decision. Still, in order to have a useful definition, two side conditions should be observed: (1) integration over all regions must reproduce the standard expression of the chemical potential and (2) enlarging the region within which the local chemical potential is defined must lead to the standard chemical potential.

In order to be compatible with the general definition of the chemical potential, that is, in order to fulfill the first side condition, the local chemical potential $\mu_{\mathrm{local}}(k,V)$ must fulfill the relation

$$\mu(C) = \int_0^{\infty} P(k,V,C)\mu_{\mathrm{local}}(k,V)\,\mathrm{d}V$$

$$\mu(C) = \int_0^{\infty} \frac{(V\cdot C)^k \exp(-V\cdot C)\cdot C}{k!}\mu_{\mathrm{local}}(k,V)\,\mathrm{d}V \tag{4}$$

which must hold for all concentrations $C$. Via the expression

$$\mu(C) = \frac{C^{\mathrm{k}}\cdot C}{k!}\cdot\int_0^{\infty}\exp(-V\cdot C)V^{\mathrm{k}}\mu_{\mathrm{local}}(k,V)\,\mathrm{d}V$$

we recognize that $\mu(C)$ can be understood as Laplace transformed of the function $V^k\mu_{\mathrm{local}}(k,V)$ multiplied by the factor $(C^k\cdot C)/k!$ . Thus, in principle, the local chemical potential can be computed by evaluating the inverse Laplace transformed of the expression

$$\frac{k!}{C^k\cdot C}\cdot\mu(C) \tag{5}$$

containing the familiar chemical potential of the homogeneous macroscopic system.

In the following, we investigate the special case that the local chemical potential is given by a trial function which depends on the ratio $k/V$

$$\mu_{\mathrm{local}}^{\mathrm{trial}}(k/V) = RT\ln(k/V)$$

Inserting this expression into the above integral yields

$$\mu(C) = RT\int_0^{\infty}\frac{(V\cdot C)^k\exp(-V\cdot C)\cdot C}{k!}\ln(k/V)\,\mathrm{d}V$$

The integral can be evaluated in closed form as

$$\mu(C) = RT\left(\ln(C) + \ln(k) - \Psi(k) - \frac{1}{k}\right) = RT\ln(C) + RT\left(\ln(k) - \Psi(k) - \frac{1}{k}\right)$$

where $\Psi(k)$ is the digamma function. The $k$-dependent term can be expanded to very good accuracy as

$$\ln(k) - \Psi(k) - \frac{1}{k} = -\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4} + O\left(\frac{1}{k^6}\right)$$

The relative deviation between the expression and its expansion is $5\times10^{-3}$ for $k=1$ and $2.5\times10^{-4}$ for $k=2$ and vanishes rapidly for increasing $k$. As we will see that for our applications the values for $k$ are in the range of 30 or higher, we can employ the series expansion throughout the following treatment

$$\mu(C) = RT\ln(C) + RT\left(-\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4}\right)$$

Thus, by assigning to the local chemical potential the expression

$$\mu_{\mathrm{local}}^{\mathrm{trial}}(k,V) = RT\ln(k/V)$$

we reproduce the ideal behavior of the macroscopic chemical potential but augmented by a constant which depends on the choice of $k$. If we redefine the local chemical potential as

$$\mu_{\mathrm{local}}(C) = RT\ln(k/V) - RT\left(-\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4}\right) \tag{6}$$

we obtain with

$$\mu(C) = RT\int_0^{\infty}\frac{(V\cdot C)^k\exp(-V\cdot C)\cdot C}{k!}\left(\ln(k/V) - \left(-\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4}\right)\right)\mathrm{d}V = RT\ln(C)$$

the ideal relationship between the chemical potential and the concentration. If we enlarge the region within which the local chemical potential is defined according to eq 6, we note that $\mu_{local}(C)$ converges toward the standard chemical potential $\mu(C)$ as required by the second side condition stated above in the text preceding eq 4.

After having defined the local chemical potential, we are in the position to calculate the chemical potential of all surfactant molecules which are, according to the above definition, in the monomer state. We have

$$\mu_{mono}\left(C\right) = \int_{V_{thres}}^{\infty} P\left(k_{thres}, V, C\right) \cdot \mu_{local}\left(k_{thres}/V\right) \mathrm{d}V \times \left(\int_{V_{thres}}^{\infty} P(k_{thres}, V, C)\, \mathrm{d}V\right)^{-1} \quad (7a)$$

or

$$\mu_{mono}(C) = X_{mono}{}^{-1} \cdot \int_{V_{thres}}^{\infty} P(k_{thres}, V, C) \cdot \mu_{local}(k_{thres}/V)\, \mathrm{d}V \quad (7b)$$

With the substitution $\tau = 1/V$, we get

$$\mu_{mono}(C) = X_{mono}{}^{-1} \cdot \int_{0}^{1/V_{thres}} P(k_{thres}, 1/\tau, C) \cdot \mu_{local}(k_{thres} \cdot \tau) \frac{1}{\tau^2}\, \mathrm{d}\tau$$

which is more suited for numerical computation.

Specializing to the expression discussed above for the local chemical potential

$$\mu_{local}(C) = RT \ln(k/V) - RT\left(-\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4}\right)$$

yields

$$\mu_{mono}(C) = X_{mono}{}^{-1} \cdot RT \int_{0}^{1/V_{thres}} P(k_{thres}, 1/\tau, C)\left(\ln(k_{thres} \cdot \tau) - \left(-\frac{1}{2k_{thres}} + \frac{1}{12k_{thres}{}^2} - \frac{1}{120k_{thres}{}^4}\right)\right) \frac{1}{\tau^2}\, \mathrm{d}\tau$$

If we use $\mu_{mic}$ as reference and assume that the monomers take on this value of the chemical potential at the concentration $C_{crit}$, we get

$$\mu_{mono}(C) = X_{mono}{}^{-1} \cdot RT \int_{0}^{1/V_{thres}} P(k_{thres}, 1/\tau, C)\left(\ln\left(\frac{k_{thres} \cdot \tau}{C_{crit}}\right) - \left(-\frac{1}{2k_{thres}} + \frac{1}{12k_{thres}{}^2} - \frac{1}{120k_{thres}{}^4}\right)\right) \frac{1}{\tau^2}\, \mathrm{d}\tau + \mu_{mic}$$

The expression for the overall chemical potential in the system

$$\mu(C) = X_{mono}(C)\mu_{mono}(C) + X_{mic}(C)\mu_{mic}$$

develops then into

$$\mu(C) = RT \int_{0}^{1/V_{thres}} P(k_{thres}, 1/\tau, C)\left(\ln\left(\frac{k_{thres} \cdot \tau}{C_{crit}}\right) - \left(-\frac{1}{2k} + \frac{1}{12k^2} - \frac{1}{120k^4}\right)\right) \frac{1}{\tau^2}\, \mathrm{d}\tau + X_{mono}(C) \cdot \mu_{mic} + X_{mic}(C) \cdot \mu_{mic}$$

$$\mu(C) = RT \int_{0}^{1/V_{thres}} P(k_{thres}, 1/\tau, C)\left(\ln\left(\frac{k_{thres} \cdot \tau}{C_{crit}}\right) - \left(-\frac{1}{2k_{thres}} + \frac{1}{12k_{thres}{}^2} - \frac{1}{120k_{thres}{}^4}\right)\right) \frac{1}{\tau^2}\, \mathrm{d}\tau + \mu_{mic} \quad (8)$$

This is the expression which has to be compared with the experimental value of the chemical potential as evaluated via the Gibbs equation.

**Model 2.** In the second model, we keep the volume $V_{thres}$ constant and ask for the probability that the number of surfactant molecules $k$ within this volume exceeds a threshold value $k \geq k_{thres}$. Again, we start with the Poisson distribution

$$P_{Poisson}(k, V, C) = \frac{(V \cdot C)^k \exp(-V \cdot C)}{k!}$$

While in the first model, all situations considered did contain the same number of surfactant molecules $k_{thres}$, in the present model, we compare situations with different number of surfactant molecules. The contributions of the different situations to the chemical potential have to be multiplied by the number of molecules. Thus, we have to multiply the Poisson distribution by $k$ in order to obtain the proper weighting function. The infinite sum evaluates to

$$\sum_{k=1}^{\infty} P_{Poisson}(k, V, C) \cdot k = VC$$

Therefore, we define the weighting function by

$$P(k, V, C) = P_{Poisson}(k, V, C) \cdot \frac{k}{VC} = \frac{(V \cdot C)^{(k-1)} \exp(-V \cdot C)}{(k-1)!} \quad (9)$$

which is normalized as

$$\sum_{k=1}^{\infty} P(k, V, C) = 1$$

For fixed $V_{thres}$, the probability $P(k,V,C)$ allows us to compute the probability to find a number of $k$ surfactant molecules and, thus, the local concentration $k/V_{thres}$. Situations with a local concentration above $k_{thres}/V_{thres}$ shall contribute to micelle formation while situations with smaller local concentration are considered to lead to monomers.

In order to compute the chemical potential of the monomers, we must have an expression for the local chemical potential. We define the trial function

$$\mu_{local}^{trial}(k, V) = RT \ln(k/V)$$

The expression

$$\sum_{k=1}^{\infty} P(k, V, C) \cdot \mu_{local}^{trial}(k, V) = RT \sum_{k=1}^{\infty} P(k, V, C) \ln(k/V)$$

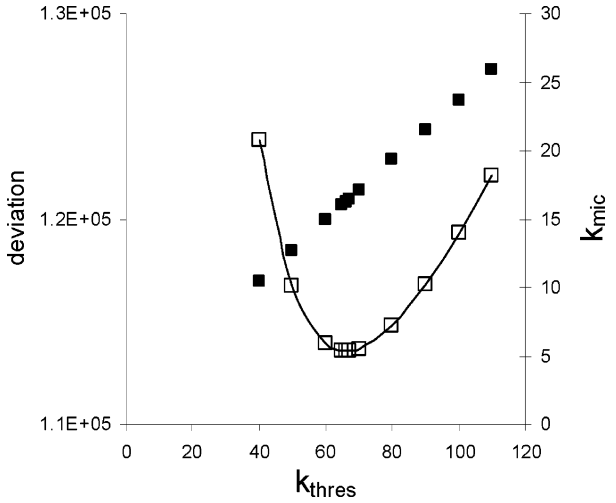


**Figure 2.** Fit within model 1. The number $k_{thres}$ of surfactant molecules involved in micelle formation is kept constant during the fit. The deviation (squares) is plotted as function of $k_{thres}$. The minimum deviation is found for $k_{thres} = 66$. The number of surfactant molecules in the micelle is computed via $k_{mic} = k_{thres} - C_{crit} \cdot V_{thres}$.

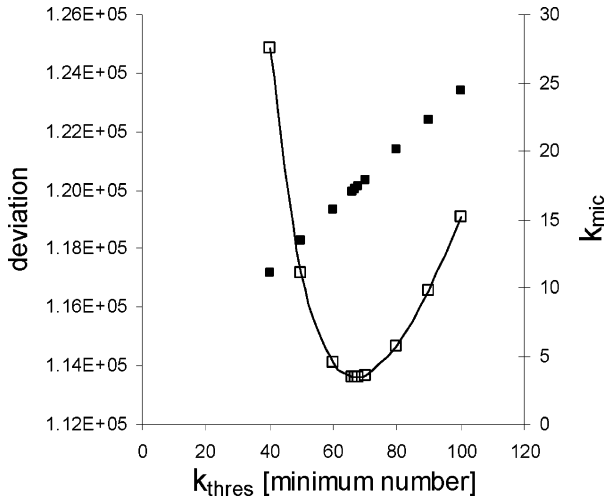


**Figure 3.** Fit within model 2. $k_{thres}$ represents here the minimum number of surfactant molecules involved in micelle formation. During the fit, the volume $V_{thres}$ has been kept constant. The deviation (squares) is plotted as function of $k_{thres}$. The minimum deviation is found for $k_{thres} = 67$. The number of surfactant molecules in the micelle is computed via $k_{mic} = k_{thres} - C_{crit} \cdot V_{thres}$.

should describe the general chemical potential. Unfortunately, we have not been able to carry out the infinite summation in closed form. The numerical evaluation of the sum leads to a value that differs from the ideal behavior. We define the difference

$$\Delta\mu(C) = RT\left(\sum_{k=1}^{\infty} P(k,V,C)\,\ln(k/V) - \ln(C)\right)$$

By setting

$$\mu_{local}(k,V) = \mu_{local}^{trial}(k,V) - \Delta\mu(C) = RT\ln(k/V) - \Delta\mu(C) \quad (10)$$

we have constructed the local chemical potential in a way that leads via

$$\mu(C) = \sum_{k=1}^{\infty} P(k,V,C)\cdot\mu_{local}(k,V) = RT\ln(C)$$

to the global chemical potential $\mu(C)$ with ideal behavior as long as only monomers are present in the system.

As in model 1, we assume that micelles are formed in regions with particularly high local concentration. We have no a priori knowledge about how big this local concentration has to be and how large the volume of the region has to be.

We define a volume $V_{thres}$ for the region, and we define a threshold value $k_{thres}$ of molecules that must be present within this volume to cooperatively lead to the formation of a micelle.

The probability for this to happen can then easily be calculated as

$$X_{mic} = \sum_{k=k_{thres}}^{\infty} P(k,V_{thres},C) \quad (11a)$$

while the probability that too few molecules are concentrated within $V_{thres}$ to cause nucleation of a micelle is given as

$$X_{mono} = \sum_{k=1}^{k_{thres}} P(k,V_{thres},C) \quad (11b)$$

The two quantities add to unity. As in model 1, they can be considered as molar fraction $X_{mic}$ of surfactant molecules being involved in micelle formation and as molar fraction $X_{mono}$ of surfactant molecules that are definitely in the state of monomers. We point out again that $X_{mic}$ does not measure the amount of surfactant molecules within micelles, but rather the molecules being involved in micelle formation.

Now, we consider the chemical potential of the surfactant molecules as function of concentration $C$. We assume that the contribution of monomer surfactant molecules to the chemical potential differs from the contribution of those surfactant molecules that are involved in micelle formation. The latter shall have the chemical potential $\mu_{mic}$ while the monomers have a chemical potential $\mu_{mono}(C)$ which depends on the concentration $C$. The chemical potential of the surfactant in the system is then given as

$$\mu(C) = X_{mono}(C)\mu_{mono}(C) + X_{mic}(C)\mu_{mic}$$

After having defined the local chemical potential, we are in the position to calculate the chemical potential of all surfactant molecules which are, according to the above definition, in the monomer state. We have

$$\mu_{mono}(C) = \sum_{k=1}^{k_{thres}} P(k,V_{thres},C)\mu_{local}(k/V_{thres})\cdot\left(\sum_{k=1}^{k_{thres}} P(k,V_{thres},C)\right)^{-1}$$

or

$$\mu_{mono}(C) = X_{mono}{}^{-1}(C)\cdot\sum_{k=1}^{k_{thres}} P(k,V_{thres},C)\mu_{local}(k/V_{thres})$$

If we use $\mu_{mic}$ as reference and assume that the monomers take on this value of the chemical potential at the concentration $C_{crit}$, we get

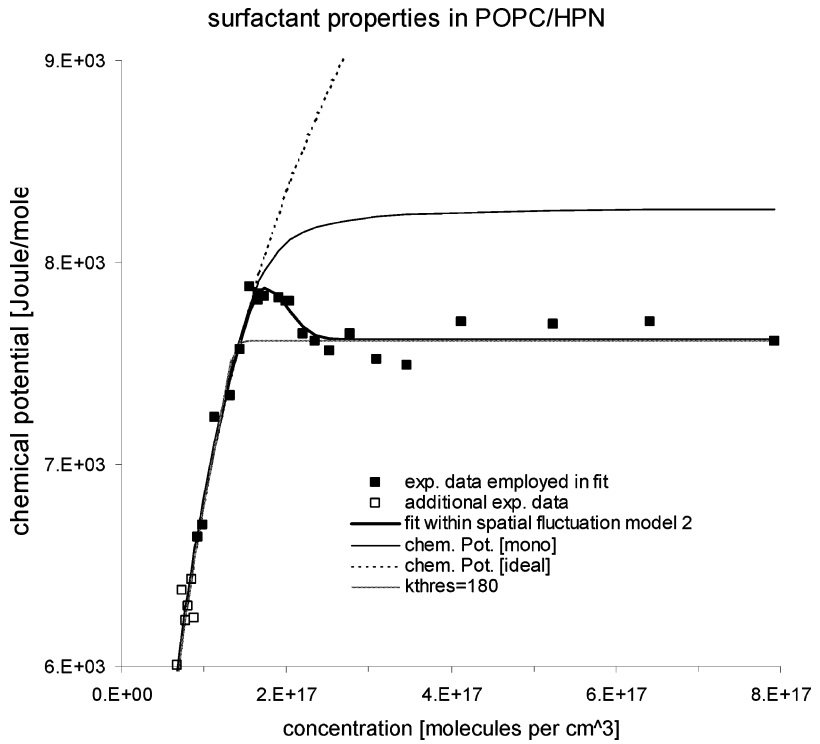


**Figure 4.** Parameters $V_{thres}$, $k_{thres}$, $C_{crit}$, and $\mu_{mic}$ have been adjusted to optimize the agreement between the experimental values of the chemical potential and the expression from eq 13. Thick line: the best fit of the chemical potential within model 2. Dashed line: chemical potential for the ideal solution. Thin line: chemical potential $\mu_{mono}(C)$ according to eq 12. Dotted line: for comparison, the calculation has been carried out after setting $k_{thres} = 180$ and $V_{thres} = 1.14 \times 10^{-15}$ cm$^3$. This setting makes the local maximum of the chemical potential vanish while leaving the micelle size $k_{mic} = 17$ constant.

$$\mu_{mono}(C) = X_{mono}{}^{-1}(C)\cdot \sum_{k=1}^{k_{thres}} P(k,V_{thres},C)(\mu_{local}(k/V_{thres}) - \mu_{mic}) + \mu_{mic} \quad (12)$$

The expression for the overall chemical potential in the system

$$\mu(C) = X_{mono}(C)\mu_{mono}(C) + X_{mic}(C)\mu_{mic}$$

develops then into

$$\mu(C) = \sum_{k=1}^{k_{thres}} P(k,V_{thres},C)(\mu_{local}(k/V_{thres}) - \mu_{mic}) + X_{mono}(C)\cdot\mu_{mic} + X_{mic}(C)\cdot\mu_{mic}$$

or

$$\mu(C) = \sum_{k=1}^{k_{thres}} P(k,V_{thres},C)(\mu_{local}(k/V_{thres}) - \mu_{mic}) + \mu_{mic} \quad (13)$$

This is the expression which has to be compared with the experimental value of the chemical potential as evaluated via the Gibbs equation.

### Results: Fit to Experimental Data

**General Remarks.** Table 1 contains the key quantities of both models. In both cases, we have four parameters, $k_{thres}$, $V_{thres}$, $C_{crit}$, $\mu_{mic}$, which are to be determined by comparison with experimental data. In principle, one could try to optimize all four parameters in one step. In practice, the fit has been carried out in the following way.

For model 1, the parameter $k_{thres}$ has been selected and kept at a fixed value while the other three parameters were varied to give the best least-squares fit to the data. It is observed that the

**TABLE 1**

| quantity | model 1 | model 2 |
|---|---|---|
| CMC | $C_{crit}$ | $C_{crit}$ |
| $\mu$ at largest conc. | $\mu_{mic}$ | $\mu_{mic}$ |
| region for micelle formation | $V \le V_{thres}$<br>$k = k_{thres}$ | $V = V_{thres}$<br>$k \ge k_{thres}$ |
| $X_{mono}$ | eq 2a: $X_{mono} = \int_{V_{thres}}^{\infty} P(k_{thres},V,C)\,dV$ | eq 11a: $X_{mono} = \sum_{k=1}^{k_{thres}} P(k,V_{thres},C)$ |
| $X_{mic}$ | eq 2b: $X_{mono} = \int_{V_{thres}}^{\infty} P(k_{thres},V,C)\,dV$ | eq 11b: $X_{mic} = \sum_{k=k_{thres}}^{\infty} P(k,V_{thres},C)$ |
| $\mu(C)$ | eq 8:<br>$\mu(C) = \mu_{mic} +$<br>$RT \int_0^{1/V_{thres}} P(k_{thres},1/\tau,C)\cdot M\cdot 1/\tau^2\,d\tau$<br>where<br>$M = (\ln(k_{thres}\cdot\tau/C_{crit}) - K)$<br>$K = (-1/2k_{thres} + 1/12k_{thres}^2 - 1/120k_{thres}^4)$ | eq 13:<br>$\mu(C) = \mu_{mic} +$<br>$\sum_{k=1}^{\kappa_{\tau\eta\rho\epsilon\sigma}} \Pi(\kappa,\zeta_{\tau\eta\rho\epsilon\sigma},X)(\mu_{local}(\kappa/\zeta_{\tau\eta\rho\epsilon\sigma}) - \mu_{mic})$<br>where<br>$\mu_{local}(k,V) = RT\ln(k/V) - \Delta\mu(C)$<br>with<br>$\Delta\mu(C)$ from numerical calculation |

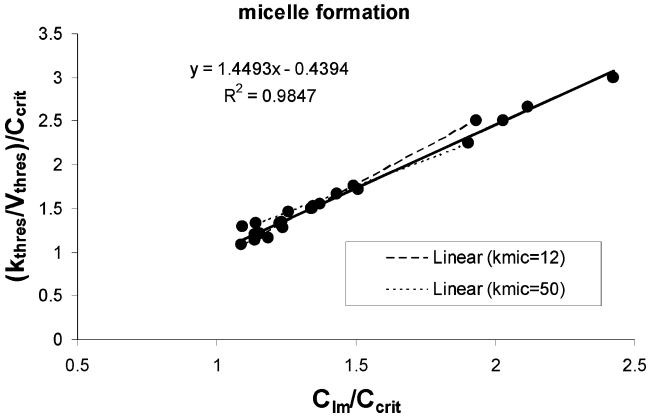


**Figure 5.** $(k_{thres}/V_{thres})\cdot C_{crit}^{-1}$ as a function of the ratio $C_{lm}/C_{crit}$. The data are computed for micelle sizes between $k_{mic} = 12$ and $k_{mic} = 50$. The dependence on the micelle size is demonstrated by the two linear fits which refer separately to two subsets.

optimized deviation between fit and data passes through a minimum as a function of $k_{thres}$; see Figure 2. The value of $k_{thres}$ with the smallest deviation and the corresponding values of $V_{thres}$, $C_{crit}$, $\mu_{mic}$ are considered to represent the data best.

For model 2, the parameter $V_{thres}$ has been kept at a fixed value while the other three parameters were varied. Again, the deviation passes through a minimum as a function of $V_{thres}$; see Figure 3. The value of $V_{thres}$ with the smallest deviation and the corresponding values of $k_{thres}$, $C_{crit}$, $\mu_{mic}$ are considered to represent the data best.

Once these parameters are obtained, one can try to draw conclusions on the behavior of the system near and above the CMC. $C_{crit}$ is the concentration where $\mu_{mono}(C)$ and $\mu_{mic}$ coincide. The ratio $k_{thres}/V_{thres}$ gives a lowest local concentration which leads to micelle formation. If a micelle is formed within the volume $V_{thres}$, then the spatial extent of the micelle is much smaller than $V_{thres}$. This means that not all surfactant molecules within $V_{thres}$ can be part of the micelle, because this would create a fairly large volume void of surfactant molecules. The concentration around the micelle must be $C_{crit}$ in order to maintain the chemical potential around the micelle identical to the chemical potential within the micelle. Thus, the number of molecules that can build the micelle is

$$k_{mic} \geq k_{thres} - C_{crit}\cdot V_{thres}$$

**Best Fit within Models 1 and 2.** The requirement that micelles are formed only in regions with a local concentration equal or above $k_{thres}/V_{thres}$ leads to the fact that not the whole amount of surfactant molecules which exceeds the averaged concentration $C_{crit}$ is used to form micelles. Thus, the monomer concentration above the threshold is somewhat higher than $C_{crit}$. This leads necessarily to a chemical potential which exceeds slightly but noticeably the value $\mu_{mic}$. The best fit within model 2 is displayed in Figure 4. The shape of the chemical potential near the local maximum is well reproduced; see ref 6. The best fit within model 1 is almost identical and therefore not shown here. Other numerical results of the best fits are comprised in the following table. The shape of the chemical potential near the CMC can coarsely be characterized by the concentration $C_{lm}$ where the local maximum is taken on and by the maximum acquired value $\mu_{lm}$. The exceeding chemical potential $\mu_{lm} - \mu_{mic}$ and the relative value of $C_{lm}$ are found in Table 2.From the last entry in Table 2, we see that the evaluation of the shape of the chemical potential near the local maximum provides us with an estimate of the micelle size.

**TABLE 2**

| quantity | model 1 | model 2 |
|---|---|---|
| $C_{crit}$ | $1.43 \times 10^{+17}$ cm$^{-3}$ | $1.43 \times 10^{+17}$ cm$^{-3}$ |
| $k_{thres}$ | 66 | 67 |
| $V_{thres}$ | $3.47 \times 10^{-16}$ cm$^3$ | $3.47 \times 10^{-16}$ cm$^3$ |
| $C_{lm}/C_{crit}$ | 1.23 | 1.24 |
| $\mu_{lm} - \mu_{mic}$ | 260.9 Joule/mol | 260.4 Joule/mol |
| $k_{mic}$ | 16 | 17 |

In order to study which quantity has the key influence on the local maximum of the chemical potential, we have carried out several test calculations. We found that both quantities $C_{lm}/C_{crit}$ and $\mu_{lm} - \mu_{mic}$ have a distinct correlation to the ratio $k_{mic}/k_{thres}$ while there is hardly any correlation to the single parameters $k_{mic}$, $k_{thres}$, and $V_{thres}$.

In order to demonstrate that and how the presence of the local maximum of the chemical potential depends on the parameters, we have raised the value of $k_{thres}$ to 180 but kept the number of molecules per micelle constant at $k_{mic} = 17$. As $C_{crit}$ remains constant, the threshold volume $V_{thres}$ has to be adjusted according to

$$k_{mic} = k_{thres} - C_{crit}\cdot V_{thres}$$

The effect of this setting onto the shape of the chemical potential is displayed in Figure 4, the curve being denoted by $k_{thres} = 180$. The local maximum of the chemical potential has clearly vanished. Reorganizing the previous equation leads to

$$\frac{k_{mic}}{k_{thres}} = \frac{\left(\frac{k_{thres}}{V_{thres}}\right) - C_{crit}}{\left(\frac{k_{thres}}{V_{thres}}\right)}$$

which indicates that a vanishing value of $k_{mic}/k_{thres}$ reduces the value of the local threshold concentration $(k_{thres}/V_{thres})$ needed to form micelles. In the limiting case of $(k_{thres}/V_{thres}) \rightarrow C_{crit}$ the micelles develop the properties of an ordinary macroscopic phase which causes a regular phase transition at the CMC.

## Conclusions and Outlook

The statistical models presented in the paper allow rationalizing a local maximum of the chemical potential and, thus, a local minimum of the surface tension near the critical micelle concentration without needing the presence of an impurity. The concept of a local chemical potential has been introduced which varies with the value of the local density fluctuations. The conventional chemical potential is necessarily conceived as a mean value of the local chemical potential averaged over the entire system. The thermodynamic requirement that within an equilibrated system all molecules of one species must have the same chemical potential is not violated, of course.

In the literature, two different path ways to micelle formation have been discussed. While one way is the concept of a phase transition, the other way conceives the formation of aggregates as a stepwise sequential process governed by equilibrium constants.[7] This behavior would give rise to an activity coefficient changing with concentration below the CMC.[8] In the case of the system POPC/HPN, the chemical potential is ideal below the CMC. Nonetheless, we have seen that the signature of a phase transition is not taken on in this system.

The occurrence of a local maximum in the chemical potential of the surfactant indicates that we are not dealing with a standard phase transition. In contrary, only in the limit of $(k_{thres}/V_{thres})$

$\rightarrow C_{crit}$ which goes along with vanishing of the difference $\mu_{lm} - \mu_{mic}$, do the models predict the signature of a phase transition.

The possibility of an impurity induced local minimum of the surface tension has been stated in the literature, but to our knowledge, no mechanism for this phenomenon has been derived yet, even though speculations about the role of an impurity more surface active than the surfactant have been presented.[5] Based on the present results, one could speculate that a surface active impurity could somehow influence the ratio $k_{mic}/k_{thres}$ and, thus, have impact onto the shape of the surface tension. Of course, this remark is far from solving the question, but it could serve as a starting point for a mechanistic study.

As today few laboratories are in the position to measure directly the surface excess $\Gamma^e$ and, thus, can assess the chemical potential $\mu$, we have carried out model calculations in order to find out which information can be gained from the shape of the surface tension alone. In our study in ref 6, we have observed that the surface excess varies only mildly near the CMC. If we introduce the approximation that the surface excess can be considered constant, then the Gibbs equation $d\sigma = -\Gamma^e\, d\mu$ yields a linear relation between the chemical potential and the surface tension. If so, then even without knowledge of the factor $\Gamma^e$ the two discernible concentrations in the shape of the surface tension, termed c1, c2 in Figure 1b, could be identified with the concentrations $C_{crit}$ and $C_{lm}$ from the fit to the shape of the chemical potential. We are now left with the question which information can be drawn from the knowledge of the two concentrations $C_{crit}$ and $C_{lm}$. Based on our model calculations we arrive at the conclusion that the ratio between the local threshold concentration for micelle formation ($k_{thres}/V_{thres}$) and the critical micelle concentration $C_{crit}$ can be evaluated fairly well, while the micelle size $k_{mic}$ requires detailed knowledge of the chemical potential. In Figure 5, the quantity $(k_{thres}/V_{thres}) \cdot C_{crit}^{-1}$ is plotted as function of $C_{lm}/C_{crit}$. The data are reasonably well reproduced by the linear relation

$$\left(\frac{k_{thres}}{V_{thres}}\right)\cdot C_{crit}^{\ -1} = 1.45\cdot \frac{C_{lm}}{C_{crit}} - 0.44$$

The data in Figure 5 visibly scatter around the linear best fit. This is due to the fact that the micelle size $k_{mic}$ has a small but noticeable effect as demonstrated by the two linear fits to data calculated for $k_{mic} = 12$ and data calculated for $k_{min} = 50$. Still, the above linear relation does allow a first estimate on the local threshold concentration ($k_{thres}/V_{thres}$) for micelle formation that would not be possible otherwise.

Finally, we would like to point out that our study has a practical application: it can be considered as a new route to determining the size of small micelles which are difficult to measure via standard techniques. As we have noticed that the shape of the experimentally observed local maximum of the chemical potential rather than the shape of the surface tension provides the necessary information to determine the micelle size, this approach requires the direct measurement of the surface excess.

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