THERMODYNAMICS OF CONDENSATION ON SOLUBLE
NUCLEI OF COLLOIDAL SURFACTANTS

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A determination is made of the chemical potential of condensate in a drop initially formed on a nucleus consisting of a surface-active substance which is soluble in the condensate. Both nonionic and ionic surfactants are examined. The threshold chemical potential of the vapor is found for the case of condensation on soluble nuclei of colloidal surfactants. The laws of thermodynamics governing heterogeneous condensation with the participation of soluble surfactants are discussed, and it is shown that, with a high aggregation number in each micelle, the micellar nature of the solution inside the drop significantly increases the threshold chemical potential of the vapor.

When the condensation nucleus of a drop consists of a surface-active substance which is soluble in the substance of the drop, the surfactant can be in solution inside the drop not only in the form of individual molecules or ions, but also in micellar form. The solution is micellar when the concentration of the solution exceeds the critical concentration for micelle formation.

The presence of a micellar solution in the given case introduces additional difficulties into the study of the thermodynamics of condensation on soluble surfactant nuclei. At the same time, the fact that the solution is micellar makes it possible to introduce certain simplifications in the thermodynamics of the condensation process — at least for concentrations that are not too much greater than the critical concentration for micelle formation. Ultimately, the fact that the solution is micellar makes it possible to describe the thermodynamics of the process analytically.

This is the goal of the present study, which is a continuation of the investigation [1-4] of the thermodynamics of condensation on soluble nuclei. We will concern ourselves with both nonionic and ionic surfactant condensation nuclei.

Thermodynamics of Heterogeneous Condensation with the Formation of Micelles of Nonionic Surfactants in a Drop. We will use the notation employed in [1-4]. Here, a is the dimensionless surface tension of a drop determined by Eq. (4) from [1]; x is the relative concentration of the substance of the nucleus in solution inside the bulk phase of the drop; x_∞ is the relative concentration of the substance of the nucleus in solution corresponding to the concentration at which complete saturation of adsorption on the drop surface is achieved; s is the dimensionless adsorption (determined from Eq. (4) in [2]); s_∞ is dimensionless adsorption in the case of complete saturation of adsorption.

An important expression here is the equation describing the material balance in the drop

$$x = \nu_n \nu^{-1} - s\nu^{-1}, \tag{1}$$

([2], Eq. (5)), where ν_n is the total number of molecules or ions in the condensation nucleus; ν is the total number of molecules of the condensate (the substance which condenses from the vapor to form the drop).

One property of soluble colloidal surfactants is their ability to form micelles when the concentration of the solution x reaches values in excess of the critical concentration for micelle formation x_{cmc}. At $x > x_{cmc}$, a solution of such surfactants becomes micellar.

For nonionic surfactants — to which the discussion will initially be limited — a micellar solution contains three components: the solvent itself, the surfactant in the form of micelles, and the surfactant in the form of individual molecules. In this sense, solution concentration x can be regarded as a gross concentration expressed mathematically in the form

$$x = x_{cmc} + n_M x_M \tag{2}$$

Here, n_M is the aggregation number in a micelle, i.e., the number of surfactant molecules in an individual micelle; x_M is the number of micelles per molecule of solvent. The first term in (2) is the number of individual surfactant molecules per molecule of solvent. The fact that this number is nearly independent of concentration x at x > x_{cmc} within a broad range of values (when x_M > 0) — as well as the fact that the number nearly coincides with the critical concentration for micelle formation — is a consequence of the law of mass action and can be explained by the tendency of individual surfactant molecules to be converted into micelles, i.e., the tendency for concentration x_M to increase to the limit corresponding to the aggregation number n_M characteristic of the given surfactant.

To represent the pattern of behavior typical of many soluble nonionic surfactants, we will discuss the process by which solution concentration x increases so as to lead to micelle formation. There are two extreme cases possible: either x_{cmc} > x_∞, or, conversely, x_{cmc} < x_∞.

In the first case, (x_{cmc} > x_∞) the concentration x_∞ is reached first. Only then is the concentration x_{cmc} attained. In the concentration region x_∞ < x < x_{cmc}, adsorption of the surfactant will already be saturated: s = s_∞. However, the solution remains molecular — it does not contain micelles. Here, in accordance with Eq. (58) from [2], surface tension a decreases logarithmically with an increase in concentration x. Saturation of adsorption necessarily entails filling of the adsorption monolayer of the surfactant. The solution becomes micellar with the transition to the concentration region x > x_{cmc}. Adsorption remains saturated in this case. Surface tension a ceases to depend on concentration x and becomes constant: $a = a_M$. The reason for this is the constancy of the concentration of individual surfactant molecules in the solution (the first term in (2)).

In the second case (x_{cmc} < x_∞), conversely, the concentration x_{cmc} is reached first. Thus, micelle formation occurs as if the adsorption monolayer had already been filled. Despite this, adsorption becomes constant throughout the concentration region x > x_{cmc} due to the constancy of the concentration of individual surfactant molecules in the solution. However, the extent of such adsorption s_∞ (denoted by the same index ∞, for the sake of consistency) will now be less than the adsorption that would have taken place in the case of complete filling of the monolayer. Constancy of the concentration and chemical potential of individual surfactant molecules in the solution ensures that $a = a_M$, i.e., that surface tension a will be independent of concentration x. It is apparent that when x_{cmc} < x_∞, the quantity x_∞ has a formal meaning: It plays almost no role in the theory.

Let us proceed directly to construction of the thermodynamics of heterogeneous condensation in the formation of micelles of nonionic surfactants in a drop. Here, the condensate of the drop will play the role of the solvent, while the substance of the condensation nucleus will play the role of the soluble surfactant. In accordance with this, we assume that the equalities s = s_∞ and $a = a_M$ are valid throughout the concentration region x > x_{cmc}. Here, the quantities s_∞ and a_M are independent of the concentration x. This simplifies the entire investigation and even allows us to formulate the problem analytically. Besides ν_n, x_∞, s_∞, x_{cmc}, and a_M, the aggregation number n_M is also included in the set of assigned initial parameters (n_M is assumed to be independent of the concentration x).

With allowance for s = s_∞, we find from (1) and (2) that

$$x_{cmc} + n_M x_M = \nu_n \nu^{-1} - s_\infty \nu^{-1/3} \tag{3}$$

Solving the material balance equation (3) for x_M, we obtain

$$x_M = \nu_n n_M^{-1} \nu^{-1} - s_\infty n_M^{-1} \nu^{-1/3} - x_{cmc} n_M^{-1} \tag{4}$$

which expresses x_M as a function of the number of molecules ν of the condensate in the drop.

However, the chemical potential of the condensate is influenced not by the gross concentration x, but by the concentration $x_{cmc} + x_M$, i.e., by the total number of individual molecules of surfactants and micelles in the solution per

condensate molecule. Using the same reasoning as in [1] to determine the chemical potential of the condensate b_ν inside the bulk phase of the drop, we have

$$b_\nu = -(x_{cmc} + x_M) + (2/3)a_M \nu^{-1/3} \tag{5}$$

where we have taken into account that $a = a_M$. As in [1], chemical potential b_ν is expressed in thermal energy units and is reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planar.

Inserting (4) into (5), we find

$$b_\nu = -\nu_n n_M^{-1} \nu^{-1} + \frac{2}{3}(a_M + \frac{3}{2}s_\infty n_M^{-1})\nu^{-1/3} - x_{cmc}(1 - n_M^{-1}) \tag{6}$$

The character of the dependence of Eq. (6) on the variable ν is the same as for the analogous expression (3) from [1]. The thermodynamic theory of condensation developed in [1] therefore makes it easy to account for the effect of micelle formation in a drop. We need only replace the parameter ν_n by $\nu_n n_M^{-1}$ and replace a by $a_M + (3/2)s_\infty n_M^{-1}$. In the expression for b_ν, we need to also introduce an additional term which is independent of ν: $-x_{cmc}(1 - n_M^{-1})$.

Of course, this term is not included in the equation expressing the extreme character of the chemical potential of the condensate:

$$(\partial b_\nu / \partial \nu)_0 = 0 \tag{7}$$

The zero subscript characterizes values of the respective quantities at the extremum. As in [1], the extremum will be unique and, specifically, will be a maximum. The magnitude of this maximum also determines the threshold value b_{tr} of the chemical potential of the vapor.

Taking the above into account, we finally obtain the following to replace Eqs. (6) and (11) from [1]:

$$\nu_0 = (\frac{9\nu_n}{2a_M n_M + 3s_\infty})^{3/2} \tag{8}$$

$$b_{tr} = \frac{2(2a_M n_M + 3s_\infty)^{3/2}}{27\nu_n^{1/2} n_M} - x_{cmc} \frac{n_M - 1}{n_M} \tag{9}$$

The threshold value b_{tr} of the chemical potential of the vapor is expressed (as b_ν) in thermal energy units and is reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid in the case of a plane contact surface.

However, the presence of the second (negative) term in the right side of Eq. (9) means that the maximum may be negative. The maximum will obviously be positive when

$$\nu_n^{1/2} < \frac{2^{1/2} n_M^{3/2}}{27(n_M - 1)x_{cmc}}(a_M + \frac{3}{2}s_\infty n_M^{-1})^{3/2} \tag{10}$$

Since $x_{cmc} \ll 1$ and since it is usually the case that $n_M \gg 1$, the upper bound (10) of $\nu_n^{1/2}$ is very weak. We will explain below how this statement accords with the fact that the threshold chemical potential of the vapor b_{tr} must in fact be positive.

Inserting (8) into (4), we obtain

$$x_{M0} = \frac{2}{27}(\frac{n_M}{\nu_n})^{1/2}(2a_M + 3s_\infty n_M^{-1})^{1/2}(a_M - 3s_\infty n_M^{-1}) - x_{cmc} n_M^{-1} \tag{11}$$

which determines the micelle concentration in the solution inside a drop in which the condensate has a chemical potential with a maximum.

As can be seen from (2), (11), the following serve as conditions for satisfaction of the inequality $x > x_{cmc}$ at $x = x_0$ (the solution inside the drop, having a chemical-potential maximum for the condensate, is micellar)

$$a_M n_M / 3s_\infty > 1 \tag{12}$$

$$v_n^{1/2} < \frac{2^{5/2}}{27} \frac{n_M^{3/2}}{x_{cmc}} (a_M + \frac{3}{2} s_\infty n_M^{-1})^{1/2} (a_M - 3 s_\infty n_M^{-1})$$ (13)

Conditions (12) and (13) are similar to conditions (14) and (42) from [3]. At $n_M \gg 1$, however, condition (12) is much weaker than condition (14) from [3] and is thus almost always satisfied. As noted, in the case $x_{cmc} < x_\infty$, the quantity s_∞ is actually less than the value obtained with complete filling of the monolayer. This is additional evidence that condition (12) is weaker than condition (14) from [3]. At $n_M \gg 1$, condition (13) will also be much weaker than condition (42) from [3].

Conditions (12) and (13) are needed for the present study of the thermodynamics of heterogeneous condensation associated with the formation of micelles in a drop. While adopting these conditions, we note that they still by no means guarantee satisfaction of condition (10).

Along with the restrictions on the maximum value of v_n imposed by conditions (10) and (13), there is also limit on the lowest possible value of v_n. This limit is due to the requirement $x_{M0} \ll 1$ that the solution be weak. In accordance with (11), this requirement reduces to

$$v_n^{1/2} \gg \frac{2^{5/2}}{27} n_M^{1/2} (a_M + \frac{3}{2} s_\infty n_M^{-1})^{1/4} (a_M - 3 s_\infty n_M^{-1})$$ (14)

At $x_{cmc} \ll 1$, conditions (10) and (13) are compatible with condition (14).

Thermodynamics of Heterogeneous Condensation in the Formation of Micelles of Ionic Surfactants in a Drop. Now we will assume that the soluble condensation nucleus consists of an ionic surfactant and that the micelles which form inside the drop have an electric charge. For nonmicellar solutions (which we examined in [1-4]), weakness of the solution always guarantees that the electrical contributions to the chemical potential of the condensate will be small compared to the nonelectrical contributions. This was noted in [2]. For micellar solutions, with $x > x_{cmc}$, the role of electrical contributions to the chemical potential of the condensate and the threshold chemical potential of the vapor is enhanced due to the strong electric charge of the micelles (in accordance with the Debye—Hückel theory, the relative weight of the electrical contributions compared to the nonelectrical contributions is proportional to the square root of concentration and the cube of the absolute value of the charge). However, we will be interested in the concentrations and micelle charges at which the patterns of behavior of ionic and nonionic surfactants are qualitatively similar and, as before, the electrical contributions are negligible.

At $x > x_{cmc}$, a solution of an ionic surfactant already contains four components: the solvent itself, as well as the surfactant in the form of micelles and surface-active ions and counterions. For the sake of determinateness, we will assume that the surfactant is a 1-1 electrolyte. As before [1-4], we will ignore dissociation of the condensate molecules. Thus, for the gross concentration of the solution x we will have the following instead of (2):

$$x = x_1 + x_2 + n_M x_M$$ (15)

where x_1 and x_2 are the numbers of surface-active ions and counterions per molecule of condensate. We will henceforth use the subscripts 1 and 2 to denote other quantities pertaining to the surface-active ions and counterions, respectively.

We will use n_1 and n_2 to designate the aggregation number of the surface-active ions and counterions in a micelle. Together with the total aggregation number $n_M = n_1 + n_2$, an important characteristic of an ionic micelle in the present case is micelle charge multiplicity $z_M = n_1 - n_2$. As for n_M, the parameter z_M is nearly independent of x at $x > x_{cmc}$.

The condition of electrical neutrality inside the bulk phase of the drop gives an equation linking x_1, x_2, and x_M:

$$x_1 - x_2 + z_M x_M = 0$$ (16)

It is evident from (15) and (16) that $x_1 = x_2 = x_{cmc}/2$ at $x = x_{cmc}$ (when it is still true that $x_M = 0$), while the inequality $x_1 < x_2$ holds at $x > x_{cmc}$ (when it is still the case that $x_M > 0$). The law of mass action also leads to the conclusion [5, 6] that the concentration and activity of the surface-active ions decrease with an increase in gross concentration x in the region $x > x_{cmc}$. This slow decrease is accompanied by a more rapid increase in the concentration and activity of the counterions, which allows us to ignore the change in concentration x_1 in Eqs. (15) and (16) at least in the initial part of the region $x > x_{cmc}$. The quantities x_1 and x_2 are represented symmetrically (to within the sign) in these equations, and we accordingly put

$$x_1 = x_{cmc}/2 \tag{17}$$

Taking (17) into account and then solving Eqs. (15) and (16) for x_2 and x_M, we obtain

$$x_2 = \frac{z_M}{n_M + z_M} x + \frac{1}{2} \frac{n_M - z_M}{n_M + z_M} x_{cmc} \tag{18}$$

$$x_M = \frac{1}{n_M + z_M} x - \frac{1}{n_M + z_M} x_{cmc} \tag{19}$$

The mean activity of ionic surfactants increases only slightly at $x > x_{cmc}$ [5]. As in the case of nonionic surfactants, this means that adsorption of the surfactant remains nearly constant: $s = s_\infty$. Due to the condition of electrical neutrality in the surface layer, the adsorption of the surface-active ions and counterions also remains constant: $s_1 = s_2 = s_\infty/2$.

In accordance with (1), (18), and (19), we will have

$$x_2 = \frac{z_M}{n_M + z_M} (\nu_n \nu^{-1} - s_\infty \nu^{-1/3}) + \frac{1}{2} \frac{n_M - z_M}{n_M + z_M} x_{cmc} \tag{20}$$

$$x_M = \frac{1}{n_M + z_M} (\nu_n \nu^{-1} - s_\infty \nu^{-1/3}) - \frac{1}{n_M + z_M} x_{cmc} \tag{21}$$

With allowance for (17) and the equality $s_1 = s_2 = s_\infty/2$, at $x > x_{cmc}$ we obtain the following from the Gibbs adsorption equation

$$a = a_M - (s_\infty/2) \ln(2 x_2 / x_{cmc}) \tag{22}$$

(the electrical contributions to the chemical potential of the counterions are negligible).

Since the ratio a_M/s_∞ is usually much greater than unity (at least when $x_{cmc}/2 < x_2 \le x_{cmc}$), we can ignore the dependence of surface tension a on gross concentration (or on the number ν of condensate molecules) and obtain $a = a_M$ from (22) with a satisfactorily small error. If we use (20), we can reduce the double inequality responsible for this simplification $x_{cmc}/2 < x_2 \le x_{cmc}$ to the conditions

$$\nu_n \nu^{-1} - s_\infty \nu^{-1/3} > x_{cmc} \tag{23}$$

$$\nu_n \nu^{-1} - s_\infty \nu^{-1/3} \le \frac{n_M + 3 z_M}{2 z_M} x_{cmc} \tag{24}$$

Condition (24) isolates the initial part of the region $x > x_{cmc}$. Equality (17) is then also valid with a high degree of accuracy. Condition (24) also guarantees that micelle concentration x_M will not exceed the small value x_{cmc}/z_M. The latter quantity will be smaller, the greater z_M. This in turn allows us to ignore electrical corrections to the chemical potential of the condensate.

Considering that $a = a_M$ and ignoring electrical corrections, we have the following for the chemical potential of the condensate b_ν in the presence of micelles of a soluble ionic surfactant:

$$b_\nu = -(x_1 + x_2 + x_M) + (2/3) a_M \nu^{-1/3} \tag{25}$$

this expression being the analog of Eq. (5). Inserting (17), (20), and (21) into (25), we find that

$$b_\nu = -\nu_n \frac{z_M + 1}{n_M + z_M} \nu^{-1} + \frac{2}{3} (a_M + \frac{3}{2} s_\infty \frac{z_M + 1}{n_M + z_M}) \nu^{-1/3} - x_{cmc} \frac{n_M - 1}{n_M + z_M} \tag{26}$$

The character of the dependence of Eq. (26) on ν is the same as for the analogous expression (6) in the case of nonionic surfactants. At $z_M = 0$, Eq. (26) naturally changes into Eq. (6).

Instead of (8) and (9), we will have the following in the case of ionic surfactants:

$$\nu_0 = \left\{ \frac{q_{m}(z_M - 1)}{2a_M(n_M + z_M) + 3s_\infty(z_M + 1)} \right\}^{1/3} \tag{27}$$

$$b_{tr} = \frac{2[2a_M(n_M + z_M) + 3s_\infty(z_M + 1)]^{1/2}}{27\nu_n^{1/2}(z_M + 1)^2(n_M + z_M)} - x_{cmc}\frac{n_M - 1}{n_M + z_M} \tag{28}$$

Comparing Eqs. (27) and (28) with analogous expressions (8) and (9) for identical values of ν_n, a_M, and s_∞, we see that ν_0 will be larger and the threshold value b_{tr} will be smaller in the case of ionic surfactants than in the case of nonionic surfactants.

Since the critical concentration for micelle formation in the case of ionic surfactants is an average of two orders greater than in the case of nonionic surfactants [5], the role of the final, constant term in the expression for b_{tr} is enhanced in the former case. Now, instead of (10), in accordance with (28) we obtain the following as the condition for positiveness of the maximum of the chemical potential of the condensate

$$\nu_n^{1/2} < \frac{2^{1/2}(n_M - z_M)^{1/2}}{27(z_M + 1)^2(n_M - 1)x_{cmc}}(a_M + \frac{3}{2}s_\infty\frac{z_M + 1}{n_M + z_M}) \tag{29}$$

Conditions (23) and (24), responsible for satisfaction of the equality $a = a_M$, reduce to the below expressions at $\nu = \nu_0$ in accordance with (27)

$$\frac{a_M(n_M + z_M)}{3s_\infty(z_M + 1)} > 1 \tag{30}$$

$$\nu_n^{1/2} < \frac{2^{1/2}(n_M + z_M)^2}{27(z_M + 1)^2 x_{cmc}}(a_M + \frac{3}{2}s_\infty\frac{z_M + 1}{n_M + z_M})(a_M - 3s_\infty\frac{z_M - 1}{n_M + z_M}) \tag{31}$$

$$\nu_n^{1/2} \geq \frac{2^{1/2}z_M(n_M + z_M)^2}{27(z_M + 1)^2(n_M + 3z_M)x_{cmc}}(a_M + \frac{3}{2}s_\infty\frac{z_M + 1}{n_M + z_M})(a_M - 3s_\infty\frac{z_M + 1}{n_M + z_M}) \tag{32}$$

these expressions being analogs of conditions (12-14), respectively.

In the region of relatively weak micelle charges of interest to us ($z_M/n_M \ll 1$), condition (31) is much weaker than condition (29). Then conditions (29) and (32) will be compatible only with a small margin of error. According to experimental data for sodium dodecylsulfate (NaDs), we have [5, 6]: $n_M = 119$, $z_M = 9$, $a_M = 4.3$, $s_\infty = 0.9$, $x_{cmc} = 1.5 \cdot 10^{-4}$. Using this data in (29) and (32), we see that the range of values of ν_n allowed by the theory will be $1.2 \cdot 10^9 \leq \nu_n < 2.5 \cdot 10^9$.

Discussion of the Thermodynamics of Condensation on Soluble Surfactant Nuclei. Let us summarize the findings in [2-4] and the present study in regard to the thermodynamics of condensation on soluble surfactant nuclei. For the sake of generality, we will be concerned below with a drop in which the chemical potential of the condensate is not necessarily maximal (or extreme). Accordingly, the number ν of condensate molecules may be arbitrary and may differ from the value ν_0 which corresponds to a maximum of condensate chemical potential. Generally speaking, the value of ν_0 is ambiguous: there may be more than one maximum even in the absence of micelles [4]. The chemical potential of the condensate may also have minima [3-4], but the latter are not of physical interest for the theory of condensation. The number ν_n of molecules or ions in a condensation nucleus (an external parameter of the problem) will be assigned. In this case, the following inequality is valid

$$\partial x / \partial \nu < 0 \tag{33}$$

[2], inequality (8)). The locations of the values ν_0 of the variable ν that will yield a maximum or maxima of condensate chemical potential will be indicated later.

First let us analyze the consequences that follow from inequality (33) and the statement made at the beginning of the article that these results are essentially valid for both nonionic and ionic surfactants.

At $\nu \sim \nu_n$, when the limitation on the smallness of the concentration of the solution inside the drop

$$\nu/\nu_n \ll 1 \tag{34}$$

([1], limitation (1)) is still not observed, we can use the estimate $s\nu^{-1/3} \sim s\nu_n^{-1/3}$. We also assume that the approximate inequality $\nu_n^{1/3} \gtrsim s_\infty$ is satisfied. This inequality is roughly equivalent to the inequality

$$\nu_n^{1/3} \gg 1 \tag{35}$$

([1], inequality (37)), which expresses the requirement that the dimensions of the condensation nucleus be macroscopic. Having made the above assumption, we then see from (1) that $x > x_{cmc}$ and $s = s_\infty$ at $\nu - \nu_n$.

In accordance with (33), relative concentration x decreases with an increase in ν. However, the equality $s = s_\infty$ remains valid until attainment of $x = x_{cmc}$. As is clear from (2) and (15), the equality $x = x_{cmc}$ is attained at the value of ν at which the quantities in the right sides of (4) and (21) (for solutions of nonionic and ionic surfactants, respectively) vanish. We will designate this value as ν_I.

Thus, in the region $\nu < \nu_I$, the solution inside the drop turns out to be micellar and, accordingly, the adsorption of the substance of the condensation nucleus on the drop surface turns out to be constant.

Let us see what takes place with a further increase in ν from the value $\nu = \nu_I$. Here, in accordance with (33), concentration x will decrease from the value $x = x_{cmc}$. There may be two extreme cases: either $x_{cmc} > x_\infty$, or $x_{cmc} < x_\infty$.

If $x_{cmc} > x_\infty$, then there is a region $\nu_I < \nu < \nu_{II}$ of ν in which $x_\infty < x < x_{cmc}$ and $s = s_\infty$. The solution inside the drop is already molecular within the region $\nu_I < \nu < \nu_{II}$, but adsorption of the substance of the condensation nucleus on the surface of the drop still remains saturated (the value ν_{II} introduced for the variable ν is as representative as the previously introduced value ν_I).

Conversely, if $x_{cmc} < x_\infty$, then the region of ν in which the solution inside the drop is molecular and adsorption on the drop surface is saturated is absent. Formally, this means that $\nu_{II} = \nu_I$. The value x_∞ also has a formal meaning at $x_{cmc} < x_\infty$.

In accordance with (33), a further increase in ν from $\nu = \nu_{II}$ is accompanied by a decrease in concentration x from $x = x_\infty$ in the case $x_{cmc} > x_\infty$ and from the value $x = x_{cmc}$ in the case $x_{cmc} < x_\infty$ (when $\nu_{II} = \nu_I$). Thus, within the region $\nu > \nu_{II}$, the solution inside the drop remains molecular but $s < s_\infty$ — adsorption of the substance of the condensation nucleus on the drop surface becomes undersaturated. In the lower part of the region $\nu > \nu_{II}$ (in which ν is close to ν_{II}) the inequality $s < s_\infty$ is still relatively weak, i.e., undersaturation of adsorption is not too great. The inequality $s < s_\infty$ becomes strong in the upper part of the region $\nu > \nu_{II}$. Undersaturation of adsorption also becomes very significant.

In the regions $\nu < \nu_I$ and $\nu > \nu_I$ (which, generally speaking, include the two regions $\nu_I < \nu < \nu_{II}$ and $\nu > \nu_{II}$), the solutions inside the drop turn out to be qualitatively different: micellar and molecular. Micellar and molecular solutions inside the drop have their own expressions for the derivative $\partial b_\nu / \partial \nu$ and their own roots for Eq. (7) corresponding to a maximum of condensate chemical potential.

We will designate these roots as $\dot{\nu}_0$ and $\ddot{\nu}_0$. The values of concentration x corresponding to $\dot{\nu}_0$ and $\ddot{\nu}_0$ (x being a function of ν) will be designated as $\dot{x}_0$ and $\ddot{x}_0$. For simplicity, we will ignore the fact that the root $\ddot{\nu}_0$ and concentration $\ddot{x}_0$ may have more than one value. Such a situation is possible [4] with observance of the inequality $w > w_b$, where $w \equiv a/s_\infty$ ([4], definition (8)). Here, a is the dimensionless surface tension of the drop in the absence of adsorption, $w_b = 15.23$ ([4], Eq. (68)). The value cited for w_b is universal and is independent of the specific values of the external parameters of the problem.

The physical validity of the root $\dot{\nu}_0$ implies that $\dot{x}_0 > x_{cmc}$. Furthermore, this corresponds to conditions (12-13) for nonionic surfactants and conditions (30-31) for ionic surfactants. The physical validity of the root $\ddot{\nu}_0$ obviously implies that concentration $\ddot{x}_0$ does not exceed the concentration x_{cmc}. Violation of this restriction is most likely in the situation in which the root $\ddot{\nu}_0$ and concentration $\ddot{x}_0$ have more than one value (when the inequality $w > w_b$ is observed). In fact, it is in this situation that the concentration of the solution inside a drop in which the condensate has a maximum of chemical potential is highest [4].

When both roots $\dot{\nu}_0$ and $\ddot{\nu}_0$ are physically valid, we will have $\dot{x}_0 > \ddot{x}_0$ and — by virtue of (33) — $\dot{\nu}_0 < \ddot{\nu}_0$.

The threshold chemical potential of the vapor is determined by the greater of the maxima of the chemical potential of the condensate.

As noted above, the condensate chemical-potential maximum given by the root $\dot{\nu}_0$ may also be negative (specifically, when conditions (10) and (29) are violated). The maximum of chemical potential b_ν given by the root $\ddot{\nu}_0$ will always be positive. This is clear from the general hypothesis that, as the variable ν decreases from values $\nu = \infty$, chemical potential b_ν increases from zero, i.e., becomes positive (with retention of the molecular structure of the solution inside the drop).

Thus, even when the maximum of condensate chemical potential given by the root ν_0 is negative, the threshold chemical potential of the vapor predicted by the theory will be positive.

For the root ν_0 to exist in the case of nuclei of nonionic surfactants, conditions (12-14) must be satisfied. In the case of nuclei of ionic surfactants, these conditions are replaced by conditions (30-32). If the root ν_0 does exist and, in addition, $n_M \gg 1$, then the quantities in the right sides of (9) and (28) for the threshold value b_{tr} of the chemical potential of the vapor will exceed the values in the right sides of (40) from [3] and (81) and (85) from [4] for the threshold value b_{tr} of vapor chemical potential in the absence of micelle formation. The expressions (9) and (28) obtained in the present study in the cases of nonionic and ionic colloidal surfactants forming condensation nuclei thus also determine the threshold chemical potential of the vapor.

As a result, surface activity of the substance of the condensation nucleus significantly increases the threshold chemical potential of the vapor if the aggregation number in the micelle is high. Thus, condensation nuclei of soluble surfactants with a high aggregation number are not interesting as effective agents for the heterogeneous transformation of a slightly supersaturated vapor to the liquid-drop state. However, if such nuclei are already present in the atmosphere (as is the case, for example in the production of detergents) and if the practical problem being considered is the converse — removing these nuclei from the atmosphere for environmental or commercial reasons — then Eqs. (9) and (28) make it possible to predict the threshold value of supersaturation of vapor in the atmosphere. Above this value, the atmosphere can be selectively cleaned by heterogeneous condensation.

We should emphasize that the thermodynamic theory of condensation on soluble surfactant nuclei developed in [2-4] and the present study is sensitive to a large number of initial physicochemical parameters. These parameters can be assigned in condensation problems. They include: ν_n, x_α, x_∞, s_∞, a, x_{cmc}, a_M, n_M, and z_M. The parameter x_α used in [2-4] (and introduced by Eq. (13) in [2]) is the characteristic value of the relative concentration x of the surfactant solution. Filling of the adsorption monolayer of surfactant only begins at $x \ll x_\alpha$ and is completed at $x \gg x_\alpha$. As we have seen, the parameter s_∞ can reflect one of two circumstances in the theory — filling of the monolayer, and constancy of the concentration of individual surfactant molecules in the solution. The parameter a is the dimensionless surface tension of a drop a in the absence of adsorption.

For the conditions of practical interest — when condensation on soluble nuclei occurs with a low level of supersaturation of the vapor — drops in which the concentration of the substance of the nucleus in solution inside the drop is low play the determining role in the thermodynamics of condensation (as was noted in [1] and proven in [1-4]). This fact is expressed by condition (34), which itself plays an important role throughout [1-4] and the present study. Condition (34) is of course less restrictive when the substance of the nucleus is surface-active.

Whether the nuclei consist of surface-inactive or surface-active substances (including colloidal substances), condensation can take place on soluble nuclei in the case of a low degree of supersaturation of the vapor only when the nuclei have macroscopic dimensions. This is expressed qualitatively by condition (35), which also plays an important role throughout our study.

It was established in both [1-4] and in our investigation how the most important thermodynamic characteristic of heterogeneous condensation on soluble nuclei — the threshold chemical potential of the vapor — depends quantitatively on all of the external physicochemical parameters.

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