

CONDENSATION ON SOLUBLE NUCLEI IN THE REGION OF THEIR PARTIAL DISSOLUTION

F. M. Kuni, A. K. Shchekin, and
A. I. Rusanov

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A formulation is given for the condition that vapor condensation on soluble nuclei takes place without a barrier in the region of partial dissolution of nuclei at all chemical potentials of the vapor at which condensation takes place without a barrier in the region of complete dissolution of the nuclei. A limitation from below, sufficient for the fulfillment of the formulated condition, on the solubility of the nucleus was found in cases of molecular as well as micellar nonionic or ionic solution in the drop being formed. This limitation is shown to actually take place when the size of the condensation nuclei that is necessary for the applicability of the limitation and at the same time is of the greatest practical interest is so large that condensation is possible at low vapor saturations. The limitation obtained is of a universal nature not related to specific interpretations of disjoining-pressure isotherms and mechanisms of wetting of the condensation nucleus.

In a previous [1-6] thermodynamic and kinetic study of condensation on soluble nuclei, it was assumed that the number of molecules of condensate (which has condensed in a drop from the vapor) is so large that the dissolution of a nucleus in a drop is complete. In the region where the number of condensate molecules is not so large, the dissolution of a nucleus in a drop will, however, be partial. We are not referring to the situation in which the substance of the nucleus (for example, sulfuric acid) is miscible in all proportions with the condensate, which acts as the solvent.

This paper will examine the region of partial dissolution of a nucleus in a drop. The main objective of the paper will be to find the limitation from below on the solubility of the nucleus that is sufficient for a barrier-free condensation process in the region of partial dissolution of the nucleus at all the chemical potentials of the vapor at which condensation takes place without a barrier in the region of complete dissolution of the nucleus. This limitation will be found in all the cases treated in [1-6], when the solution of the substance of the nucleus is micellar, and the substance of the nucleus can be a nonionic or ionic colloidal surfactant. As in [1-6], it is immaterial whether the nucleus is solid or liquid. Into the theory developed in [1-6] there will thus be introduced an important characteristic of the condensation nucleus — the solubility of the substance of the nucleus, with the curvature of its surface taken into account.

Condition of barrier-free condensation in the region of partial dissolution of the nucleus. Irrespective of the regime of substance exchange (free-molecular, diffusional or intermediate) taking place between the drop and vapor, the following expression holds:

$$\dot{\nu} \geq 0 \text{ when } b_v \leq b \quad (1)$$

where ν is the number of condensate molecules and $\dot{\nu}$ is the rate of its change in time, and b_v and b are the chemical potentials of the condensate and vapor, respectively.

The maximum of the chemical potential b_v of the condensate or the largest of its maxima (if there is more than one maximum) in the range of variation of variable ν where the dissolution of the nucleus in the drop is complete was found in [1, 3-6]. The values of the quantities corresponding to this maximum will be denoted by the index zero (in [3-5] the index zero also referred to the extremes of the chemical potential of the condensate). The equality

$$b_{ir} = b_{v_0} \quad (2)$$

defines the threshold value b_{tr} of the chemical potential of the vapor in the region of complete dissolution of the nucleus. When

$$b \geq b_{tr} \quad (3)$$

dropwise condensation of the vapor takes place without a barrier in this entire range: according to (1), the inequality $\dot{\nu} > 0$ is satisfied, i.e., the drops grow uncontrollably.

In order for the value b_{tr} of the chemical potential of the vapor, found in [1, 3-6] as the maximum of the chemical potential b_v of the condensate in the region of complete dissolution of the nucleus, to guarantee for all b at which (3) takes place the satisfaction of the inequality $\dot{\nu} > 0$ also in the region of partial dissolution of the nucleus, it is necessary, according to (1), that in this entire region

$$b_v < b_{tr} \quad (4)$$

The inequality (4) gives the condition of barrier-free condensation in the region of partial dissolution of the nucleus. Only when this condition is satisfied will the value b_{tr} of the chemical potential of the vapor, found in [1, 3-6], determine the threshold of barrier-free condensation in the entire range of variation of variable ν , and not just in the region of complete dissolution of the nucleus.

Removal of the substance of the nucleus, as it dissolves in the drop as the number of molecules ν of the condensate (acting as the solvent) increases, leads to nonuniformity of the nonequilibrium concentration of the substance of the nucleus in the liquid film between the remainder of the nucleus, which has not yet been able to dissolve, and the vapor-gas medium surrounding the drop. In addition to the concentration, the chemical potential b_v of the concentrate will also be nonuniform in the liquid film. The material exchange of the drop with its surroundings is of course determined by the chemical potential b_v of the condensate on the surface of the drop (through which the exchange takes place). This potential must be kept in mind in (1) and (4).

Finding the chemical potential b_v of the condensate on the surface of the drop in the course of dissolution of the nucleus makes it necessary to solve the unsteady-state equation of diffusion of the dissolved substance of the nucleus in the liquid film of the drop with the complex boundary conditions at each instant that (1) the concentration of the desired substance of the nucleus on the surface of the remainder of the nucleus is equal to its solubility on the surface (dependent on the curvature of the surface) or, more generally, is determined by the rate of dissolution of the remainder of the nucleus, and that (2) the flow of dissolved substance on the surface of the drop is equal to the rate of change with time in the amount of substance of the nucleus adsorbed on this surface. The indicated difficulties, due to the nonequilibrium state of the substance of the nucleus, can, however, be avoided by determining when the inequality $\dot{\nu} > 0$ holds in the region of partial dissolution of the nucleus. This will be demonstrated below.

Let us assume that, as a result of absorption of vapor molecules by the drop, an increase in the chemical potential b_v of the condensate will take place on the surface of the drop. This will cause an increase in the release of vapor molecules by the drop into the medium surrounding it, and hence, a weakening of the inequality $\dot{\nu} > 0$, i.e., deceleration of the condensation process. This in turn will promote the establishment of an internal equilibrium of the dissolved substance of the nucleus in the drop and the establishment of an adsorption equilibrium on the surface of the drop and an equilibrium with the remainder of the nucleus, whose size will adjust to both equilibria.

Thus, the breakdown of the inequality $\dot{\nu} > 0$ should be preceded by a near-equilibrium situation in which the concentration of the dissolved substance of the nucleus in the drop is practically uniform and equal to the solubility of the remainder of the nucleus. To this solubility can be referred the chemical potential b_v of the condensate in the condition (4). If in addition, the condition (4) is satisfied, the inequality $\dot{\nu} > 0$ will not breakdown.

By concentration of the dissolved substance of the nucleus will be meant its relative concentration, i.e., the number of molecules or ions of the dissolved substance of the nucleus per condensate molecule. This concentration will (as was in done [3-5]) be denoted by x and referred to simply as concentration of the solution. The equilibrium concentration at the surface of the nucleus will be denoted by x_n and referred to as the solubility of the nucleus. It is related to the solubility x_{sol} of the substance of the nucleus at a flat surface by the Ostwald-Freundlich formula, $x_n = x_{sol} \cdot \exp(2\gamma_n \nu_n / R_n kT)$, where γ_n is the mechanical surface tension of the nucleus, ν_n is the molecular volume of the substance of the nucleus, R_n is the radius of the nucleus (initially present in the vapor-gas medium), T is the temperature, and k is Boltzmann's constant. When the mechanical surface tension is positive, obviously $x_n > x_{sol}$. If the substance of the nucleus is miscible with the condensate in all proportions, we have

$$x_{\text{sol}} = 0 \text{ and } x_n = \infty.$$

As was shown above, when the nucleus undergoes partial dissolution, the solution concentration x may be assumed in the condition (4) to be equal to the solubility of the remainder of the nucleus. Since the surface curvature of the remainder of the nucleus is greater than the surface curvature of the nucleus (initially present in the vapor – gas medium), we have

$$x > x_n \quad (5)$$

In the region of the variable ν , where the dissolution of the nucleus is partial and the solution concentration x may fail to satisfy the inequality $x \ll 1$, one can no longer assume that the drop radius R is proportional to $\nu^{1/3}$ (as was done in formula (2) of [1] and in the formulas based on it). Sufficient for the entire discussion below will be the inequality

$$R > R_n, \quad (6)$$

which is always applicable.

The inequalities (5) and (6) greatly simplify the discussion and make it possible to establish in analytic form the limitation on the solubility x_n from below, sufficient for the fulfillment of the condition (4). Despite the fact that the limitation will not allow for the disjoining pressure of the liquid film in the drop, pressure which would lead to an attenuation of the limitation, this limitation will nevertheless prove to be realistic — actually realizable at such large sizes of the condensation nuclei, necessary for the applicability of the limitation and at the same time, most interesting from a practical standpoint, that condensation is possible at low vapor supersaturations.

The fact that the limitation on x_n from below does not take into account the disjoining pressure of the liquid film, even though it takes into consideration the fact of the weakening effect of this pressure on the limitation, it provides for the universal character of the limitation; this character is related to specific representations of the disjoining-pressure isotherms and of the mechanisms of wetting of the condensation nucleus.

The sizes of the condensation nuclei necessary for the applicability of the limitation are due to the assumption, necessary in its derivative, of diluteness of the solution in the drop, and, in the case of a micellar solution of ionic surfactants, also due to the required stronger assumption that the electric interaction of charged micelles is slight in the drop. It is essential, however, that the required assumptions be valid at the solution concentration specifying the lower bound of the limitation on x_n . If this does in fact occur, the fulfillment of the condition (4) is guaranteed at the solution concentration specifying the lower bound of the limitation on x_n . But then, the fulfillment of the condition (4) will also be guaranteed at higher solution concentrations (at which the required assumptions are no longer valid). This is a thermodynamic consequence of the stability of the solution, whereby the chemical potential of the solvent (whose role is played by the condensate) decreases as the solution concentration increases. Thus the desired limitation on the concentration x_n from below is not related to whether or not the assumptions of diluteness of the solution in the drop and smallness of the electric interaction therein are valid at all concentrations x_n satisfying this limitation.

The larger the size of the condensation nucleus, the lower, as will be ascertained below, the solution concentration specifying the lower limit of the limitation on x_n . When the size of the condensation nucleus is sufficiently large, the assumptions of diluteness of the solution in the drop and smallness of the electric interaction in the drop inevitably take effect at the lower limit of the limitation itself will take effect.

Limitation on solubility in the case of a molecular solution. Let us find the limitation on x_n from below sufficient for the fulfillment of the condition (4). We start with the case in which the substance of the nucleus is surface-inactive. In the region of complete dissolution of the nucleus, the solution concentration x in the drop will then be determined by the equality $x = \nu_n/\nu$, where ν_n is the number of molecules or ions of the nucleus (initially present in the vapor – gas medium).

According to formula (3) we have from [1]

$$b_{\nu_0} = -x_0 + (2/3) a\nu_0^{-1/3} \quad (7)$$

where a is the dimensionless surface tension of the drop (determined by Eq. (4) from [1]). The chemical potential b_ν of the concentrate and b of the vapor are expressed (as in [1-6]) in thermal units of energy and reckoned from the value corresponding to the equilibrium of the vapor and condensing liquid at the flat surface of their contact.

For the threshold value b_{tr} of the chemical potential of the vapor, determined by the equality (2), we have

$$b_{tr} = 2 (2a)^{3/2} / 27 v_n^{1/2} \quad (8)$$

([1], formula (11)).

According to $x_0 = \nu_n / \nu_0$ and the expression (6) for ν_0 from [1], the condition

$$x_0 \ll 1 \quad (9)$$

of diluteness of the solution in the drop when $\nu = \nu_0$, assumed in Eqs. (7) and (8), requires

$$v_n^{1/2} \gg (2a)^{3/2} / 27 \quad (10)$$

Since it is written directly in terms of ν_0 , the condition (9) will be

$$v_n / v_n \ll 1 \quad (11)$$

For the strong inequality (10) to be satisfied, it is essentially sufficient that the following approximate inequality be obeyed:

$$v_n^{1/3} \geq 2a/3 \quad (12)$$

which will be taken instead of (10) as the condition of applicability of the theory developed in [1].

In the region of complete dissolution of the nucleus, the chemical potential b_v of the condensate is made up [1, 3-6] of two contributions. The first contribution, always negative, describes the influence on the condensate of the substance of the nucleus dissolved therein. The second contribution, always positive, describes the influence on the condensate of the capillary pressure produced by the surface of the drop. Both of these contributions are also present in the region of partial dissolution of the nucleus. Added to them, however, is also a third contribution describing the influence on the condensate of the disjoining pressure of the liquid film in the drop. This contribution is always negative and therefore conducive to the fulfillment of the condition (4).

Taking into consideration the fact that the contribution to b_v from the disjoining pressure is negative, assuming the dilute-solution approximation, in which the contribution to b_v from the solution concentration is $-x$, and taking into account the inequality (5) in the estimate of this contribution and the inequality (6) in the estimate of the contribution to b_v from capillary pressure, we have the following inequality in the region partial dissolution of the nucleus:

$$b_v < -x_n + (2/3) a v_n^{-1/3} \quad (13)$$

where, for simplicity, the coefficient of proportionality between R_n and $\nu_n^{1/3}$ is assumed to be approximately equal to the coefficient of proportionality between R_0 and $\nu_0^{1/3}$.

According to (8) and (13), the following expression will be sufficient for the fulfillment of the condition (4)

$$x_n > \frac{2a}{3v_n^{1/3}} \left[1 - \frac{2(2a)^{1/2}}{9v_n^{1/6}} \right] \quad (14)$$

which imposes the desired limitation on the solubility x_n from below. Since the limitation (14) provides for the fulfillment of the condition (4) even when in (13) the inequality sign is replaced by an equality sign, it is evident from (2), (4), (7), and (11) that the limitation (14) additionally guarantees the inequality

$$x_0 < x_n \quad (15)$$

which is consistent with the fact that x_0 (as was assumed) lies in the region of complete dissolution of the nucleus.

From the approximate inequality (12), the following approximate inequalities are obvious:

$$2a/3v_n^{1/3} \leq 1 \quad (16)$$

$$2(2a)^{1/2}/9v_n^{1/6} \leq 2/3^{1/2} \quad (17)$$

They show that the solution concentration specifying the lower limit of the limitation (14) on x_n decreases, and the limitation (14) itself is correspondingly attenuated as ν_n increases in the entire region of applicability of the theory developed in [1] (a region defined by the approximate inequality (12)). The inequalities (16) and (17) also show that at the applicability limit of this theory, when the limitation (14) becomes most stringent, it represents

$$x_n \geq 1 - 2/3^{3/2} \quad (18)$$

The condition (12) of applicability of the theory in the region of complete dissolution of the nucleus does not, however, provide for the applicability of the limitation (14). It is necessary, in accordance with what was stated in the preceding section of this paper, that the concentration specifying the lower bound of the limitation (14) be much smaller than unity (only then will the assumption, used in the derivation of the limitation (14), of diluteness of the solution in the drop be justified). As is clear from (14), this necessitates that

$$\nu_n^{1/3} \gg 2a/3 \quad (19)$$

which is the condition of applicability of the limitation (14). This condition is stronger than the condition (12). When the condition (19) is satisfied, the limitation (14) becomes very weak: it even allows very low solubilities x_n (which are much smaller than unity).

The condition (19) is completely acceptable for such large sizes of condensation nuclei, most interesting for practical purposes, for which condensation is possible at low supersaturations of the nucleus.

The limitation (14), when the condition (19) of its applicability is obeyed, reduces with a high degree of accuracy to

$$x_n > \frac{2a}{3\nu_n^{1/3}} \quad (20)$$

which, as is evident from (13), is sufficient for the fulfillment of not only the condition (4), but also the stronger condition $b_v < 0$ in the entire region of partial dissolution of the nucleus. According to (1), in this entire region, condensation will then take place without a barrier even when $b > 0$ (and not just when the inequality (3) applies).

In a situation typical of water vapor in the earth's atmosphere and of the condensation nuclei present therein, when $a \approx 10$ and $\nu_n^{1/3} \gtrsim 10^2$ ($R_n \gtrsim \times 10^{-6}$ cm), the condition (19) is closely obeyed. The limitation (20) in this case means that $x_n \gtrsim 7 \times 10^{-2}$. It takes place, for example, for granules of the salts NaCl and CsI, which may reach the earth's atmosphere in large quantities as a result of natural processes or disasters.

The fact that for small condensation nuclei for which $\nu_n^{1/3} \lesssim 10^2$, the fulfillment of the condition (4) of barrier-free condensation in the region of partial dissolution of the nucleus may require very high solubility, which does not really occur, of the substance of the nucleus (with a concentration x_n that is appreciable compared to unity) may be one of the reasons why small nuclei of certain salts (for example, Na_2SO_4) are held for long periods in the earth's atmosphere.

Now let the substance of the nucleus be surface-active (but not form micelles in solution). The formulas thus obtained for b_{tr} in [3-5], in contrast to formula (8), are very complex. When the condition (19) is obeyed, the limitation (20) nevertheless remains applicable and provides for the fulfillment of the condition $b_v < 0$ (which does not include the quantity b_{tr} at all), which is even stronger than (4). Since the relations (2), (7), (11), and (13) are valid as before, and the limitation (20) provides for the fulfillment of the condition $b_v < 0$ even when in (13) the inequality sign is replaced by an equality sign, this limitation simultaneously guarantees the inequality (15). It is apparent from (5) and (15) that in the absence of micelles of surfactant in the region of partial dissolution of the nucleus, the solution will be molecular also when $x = x_0$. From (11), (9) now results even with a margin.

The following should also be kept in mind. In the presence of surface activity of the substance of the nucleus, the surface tension of the drop is no longer constant, but because of adsorption, is dependent on the solution concentration. Since, as the concentration of the surfactant solution increases, the surface tension decreases, it is sufficient, in the condition (19) of applicability of the limitation (20) and in this limitation itself, to replace with a margin the dimensionless surface tension a by its slightly greater dimensionless surface tension \bar{a} in the absence of adsorption, \bar{a} being independent of the solution concentration (it is a parameter of the theory).

Limitation on solubility in the case of a micellar solution of nonionic surfactants. When the solution is micellar, the concentration x acquires [6] the meaning of overall concentration. In the case of a micellar solution of nonionic surfactants, this is expressed as follows:

$$x = x_{cmc} + n_M x_M \quad (21)$$

([6], relation (2)). Here x_{cmc} is the critical overall concentration of micelle formation; n_M is the aggregation number, i.e., the number of surfactant molecules in a separate micelle; x_M is the number of micelles per molecule of solvent (whose role is played by the condensate). The relation (21) holds not only in the region of complete dissolution of the nucleus, but also in the region of its partial dissolution. In addition to x , the solubility of the nucleus x_n also has the meaning of overall concentration.

However, the chemical potential of the condensate is affected not by the overall concentration x but by the concentration $x_{cmc} + x_M$ — the total number of single molecules of surfactant and micelles in solution per molecule of condensate. According to formula (5) from [6], we then write

$$b_{v_0} = - (x_{cmc} + x_{M0}) + (2/3) a_M v_0^{-1/3} \quad (22)$$

where a_M is the dimensionless surface tension of the drop (which, like ν_n , x_{cmc} , n_M , is a parameter of the theory), independent of the concentration of the micellar solution [6].

For the threshold value b_{tr} of the chemical potential of the vapor, determined by the equality (2), we have

$$b_{tr} = \frac{2(2a_M n_M + 3s_\infty)^{3/2}}{27 n_M v_n^{1/2}} - \frac{n_M - 1}{n_M} x_{cmc} \quad (23)$$

([6], formula (9)). Here s_∞ is the dimensionless magnitude of adsorption, determined by the equality (4) from [3], in the case of its complete saturation (a parameter of the theory supplementary to ν_n , x_{cmc} , n_M , a_M). The fact that the true threshold value of the chemical potential of the vapor in the region of complete dissolution of the nucleus can, as was note in [6], be even greater than that predicted by formula (23) (it is determined by that part of the region of complete dissolution of the nucleus where micelle formation in the surfactant solution is absent) only adds weight to the following conclusions.

To be able to consider the radius of the drop in the region of complete dissolution of the nucleus as being proportional to $\nu^{1/3}$, as was assumed in (22) and (23), it is necessary that the overall concentration x be much smaller than unity. Since $n_M \gg 1$, the condition $x \ll 1$, as is clear from (21), provides with a margin for the condition $x_{cmc} + x_M \ll 1$ of diluteness of the solution, a condition that was also assumed in (22) and (23). According to (21) and the expression (11) for x_{M0} from [6], the condition $x \ll 1$ when $\nu = \nu_0$ (when it represents the previous condition (9), in which, however, x_0 has the meaning of overall concentration) requires

$$v_n^{1/2} \gg \frac{2^{3/2}}{27} n_M^{3/2} \left(a_M + \frac{3}{2} s_\infty n_M^{-1} \right)^{1/2} (a_M - 3s_\infty n_M^{-1}) \quad (24)$$

This refines the condition obtained in [6] from $x_{M0} \ll 1$ [6], condition (14).

Thanks to $n_M \gg 1$, the following expression is usually valid:

$$a_M n_M / s_\infty \gg 1 \quad (25)$$

and then (11) follows from (24) and from the expression (8) for ν_0 , given in [6]. For the strong inequality (24) to be obeyed, it then suffices that the following approximate inequality be obeyed:

$$v_n^{1/3} \geq 2a_M n_M / 3 \quad (26)$$

which we will take instead of (24) as the condition of applicability of the theory developed in [6]. The opposite limitation on ν_n from above [6], limitation (13)), necessary for the applicability of this theory and due to the fact that it is necessary to have $x_0 > x_{cmc}$ (the solution at concentration x_0 is micellar) proves, thanks to the very strong inequality $x_{cmc} \ll 1$, to be so weak that it can be completely removed from the verification below.

Despite the fact that $n_M \gg 1$, the condition (26) is acceptable at such large sizes of condensation nuclei, most interesting for practical purposes, that condensation is possible at low supersaturations of the nucleus.

It follows from (21) that

$$x_{\text{cmc}} + x_M = \frac{1}{n_M} x + \frac{n_M - 1}{n_M} x_{\text{cmc}} \quad (27)$$

and this, along with (21), is also valid in the region of both complete and partial dissolution of the nucleus. Considering that the contribution of disjoining pressure to the chemical potential b_v of the condensate is negative, using the dilute-solution approximation, in which the contribution of the solution concentration to b_v is $-(x_{\text{cmc}} + x_M)$, and considering the expression (27) and the inequality (5) in the estimate of this contribution and the inequality (6) in the estimate of the contribution of capillary pressure to b_v , we have the following inequality in the region of partial dissolution of the nucleus:

$$b_v < - \left(\frac{1}{n_M} x_n + \frac{n_M - 1}{n_M} x_{\text{cmc}} \right) + \frac{2a_M}{3\nu_n^{1/3}} \quad (28)$$

where (as in (13)) it was assumed for simplicity that the coefficient of proportionality between R_n and $\nu_n^{1/3}$ is approximately equal to the coefficient of proportionality between R_0 and $\nu_0^{1/3}$. We emphasize that for the inequalities (6) and (28) to be applicable in this region, it is not necessary that the overall concentration x be small, i.e., that the inequality $x \ll 1$ hold in the region of incomplete dissolution of the nucleus.

According to (23) and (28), the following expression is sufficient for the fulfillment of the condition (4):

$$x_n > \frac{2a_M n_M}{3\nu_n^{1/3}} \left[1 - \frac{(2a_M n_M + 3s_\infty)^{3/2}}{9a_M n_M \nu_n^{1/6}} \right] \quad (29)$$

which imposes on the solubility x_n the desired limitation from below in the case of a micellar solution of nonionic surfactants. Since the limitation (29) provides for the fulfillment of the condition (4) even when in (28) the inequality sign is replaced by an equality sign, it is evident from (2), (4), (11), (22), and (27) that the limitation (29) simultaneously guarantees the inequality (15).

In complete analogy to (16), (17), the following approximate inequalities are clear from (25), (26):

$$\frac{2a_M n_M}{3\nu_n^{1/3}} \leq 1 \quad (30)$$

$$\frac{(2a_M n_M + 3s_\infty)^{3/2}}{9a_M n_M \nu_n^{1/6}} \leq \frac{2}{3^{3/2}} \quad (31)$$

They show that the solution concentration, which specifies the lower bound of the limitation (29) on x_n , decreases, and the limitation (29) itself correspondingly weakens as ν_n increases in the entire region of applicability of the theory developed in [6]. The inequalities (30), (31) also show that at the applicability limit of this theory, when the limitation (29) becomes most stringent, it constitutes the limitation (18).

In contrast to the case of the molecular solution, the limitation on x_n is now applicable for all ν_n at which the theory is applicable in the region of complete dissolution of the nucleus. Actually, even when the overall concentration, which specifies the lower bound of the limitation (29), reaches the maximum value allowed by the inequality (26), equal to the value on the right side of (18), there is obeyed, as is clear from (27) and the strong inequalities $n_M \gg 1$ and $x_{\text{cmc}} \ll 1$, the condition

$$x_{\text{cmc}} + x_M \ll 1 \quad (32)$$

of diluteness of the solution in the drop, assumed in the derivation of the limitation (29).

For micellar solutions, in which $n_M \gg 1$, the overall concentration x_n may be appreciable in comparison to unity. Then the limitation (29) will also take place at such ν_n that the condition (26) of its applicability only begins to take effect.

Limitation on solubility in the case of a micellar solution of ionic surfactants. For the overall solution concentration x , we have, instead of (21),

$$x = x_1 + x_2 + n_M x_M \quad (33)$$

([6], relation (15)), where x_1 and x_2 are the numbers of monomeric surface-active ions and counterions per condensate molecule. In addition to x , the solubility x_n , as before, has the meaning of overall concentration. The condition of electrical neutrality inside the volume phase of the drop gives the following relation supplementary to (33):

$$x_1 - x_2 + z_M x_M = 0 \quad (34)$$

([6], relation (16)), where z_M is the charge multiplicity of the micelle (a parameter of the theory supplementary to the parameter introduced earlier) and the ions are assumed to be singly charged. The relations (33), (34) hold independently of the completeness of dissolution of the nucleus.

The chemical potential of the condensate is affected not by the overall concentration x but by the concentration $x_1 + x_2 + x_M$ — the total number of ions, counterions and micelles in solution per condensate molecule. According to formula (25) from [6], we then write

$$b_{v_0} = - (x_{10} + x_{20} + x_{M0}) + (2/3) a_M v_0^{-1/3} \quad (35)$$

(a_M being the dimensionless surface tension of the drop, independent of the concentration of the micellar solution [6]).

For the threshold value b_{tr} of the chemical potential of the vapor, defined by the equality (2), we have

$$b_{tr} = \frac{2 \{2a_M (n_M + z_M) + 3s_\infty (z_M + 1)\}^{1/2}}{27 (z_M + 1)^{1/2} (n_M + z_M) v_n^{1/2}} - \frac{n_M - 1}{n_M + z_M} x_{cmc} \quad (36)$$

([6], formula (28)). The fact that the true threshold value of the chemical potential of the vapor in the region of complete dissolution of the nucleus can, as was noted in [6], be even higher than that predicted by formula (36) (it is determined by that part of the region of complete dissolution of the nucleus where micelle formation in a surfactant solution is absent) only lends additional weight to the subsequent conclusions.

The equality $a = a_M$ used in (35), (36) and the equality

$$x_1 = x_{cmc}/2 \quad (37)$$

used in (36) ([6], equality (17)) are certainly valid [6] in the initial portion of the region of micelle formation $x > x_{cmc}$, in which $x_2 > x_{cmc}/2$, but still $x_2 \lesssim x_{cmc}$. Also valid [6] are the condition $x_1 + x_2 + x_M \ll 1$ of solution diluteness and the stronger conditions (when $n_M \gg 1$, $z_M \gg 1$) $x \ll 1$ and $z_M^3 x_M \ll 1$, all used in (35), (36), which make it possible to consider the radius of the drop as being proportional to $\nu^{1/3}$ and to neglect the electrical interaction of charged micelles.

The inequality $x_2 > x_{cmc}/2$ requires the following when $\nu = \nu_0$:

$$\frac{a_M (n_M + z_M)}{3s_\infty (z_M + 1)} > 1 \quad (38)$$

$$v_n^{1/2} < \frac{2^{3/2} (n_M + z_M)^{3/2}}{27 (z_M + 1)^{3/2} x_{cmc}} \left(a_M + \frac{3}{2} s_\infty \frac{z_M + 1}{n_M + z_M} \right)^{1/2} \left(a_M - 3s_\infty \frac{z_M + 1}{n_M + z_M} \right) \quad (39)$$

([6], inequalities (30), (31)). The approximate inequality $x_2 \lesssim x_{cmc}$ requires the following $\nu = \nu_0$:

$$v_n^{1/2} \geq \frac{2^{5/2} z_M (n_M + z_M)^{3/2}}{27 (z_M + 1)^{3/2} (n_M + 3z_M) x_{cmc}} \left(a_M + \frac{3}{2} s_\infty \frac{z_M + 1}{n_M + z_M} \right)^{1/2} \times \left(a_M - 3s_\infty \frac{z_M + 1}{n_M + z_M} \right) \quad (40)$$

[6], approximate inequality (32)). Since usually $n_M \gg z_M \gg 1$, (38) is obeyed with a margin. The inequalities (39) and (40) are always compatible, although with a small margin. The interval, allowed by them, of the values of parameter ν_n lies within the region of such large sizes of condensation nuclei of greatest practical interest that condensation is possible at low supersaturations of the vapor. According to the experimental data for dodecyl sodium sulfate, we have [7, 8]: $n_M = 119$, $z_M = 9$, $a_M = 4.3$, $s_\infty = 1.8$, $x_{cmc} = 1.5 \cdot 10^{-4}$. The interval of ν_n values which is allowed by the inequalities (39) and (40) is $1 \times 10^9 \lesssim < 7 \times 10^{10}$ in this case.

Thanks to $n_M \gg z_M \gg 1$ and to the extremely strong inequality $x_{cmc} \ll 1$, the following inequalities usually hold:

$$a_M (n_M + z_M) / s_\infty (z_M + 1) \gg 1 \quad (41)$$

$$(n_M + 3z_M) x_{cmc} / 2z_M \ll 1 \quad (42)$$

(the inequality (41) ensures that the inequality (38) is obeyed with a margin). From (40)-(42) and expression (27) given in [6], (11) follows for ν_0 . It also follows from (41) that (40) is practically equivalent to the approximate inequality

$$\nu_n^{1/3} \gtrsim \frac{2a_M (n_M + z_M)}{9 (z_M + 1)} \left[\frac{2z_M}{(n_M + 3z_M) x_{cmc}} \right]^{2/3} \quad (43)$$

which we will keep in mind below instead of (40).

According to (33), (34), and (37), we have

$$x_2 = \frac{z_M}{n_M + z_M} x + \frac{1}{2} \frac{n_M - z_M}{n_M + z_M} x_{cmc} \quad (44)$$

$$x_M = \frac{1}{n_M + z_M} x - \frac{1}{n_M + z_M} x_{cmc} \quad (45)$$

$$x_1 + x_2 + x_M = \frac{z_M + 1}{n_M + z_M} x + \frac{n_M - 1}{n_M + z_M} x_{cmc} \quad (46)$$

(expression (44), (45) duplicate expressions (18), (19) from [6]). We assume that the inequality (37) holds not only in the region of complete dissolution of the nucleus, but also in the region of its partial dissolution (this is confirmed below). Then expressions (44)-(46) will also hold in the region of partial dissolution of the nucleus. Considering that the contribution of disjoining pressure to the chemical potential of the condensate b_ν is negative, neglecting the electrical interaction of the micelles and assuming a dilute-solution approximation in which the contribution of the solution concentration to ν_n is $-(x_1 + x_2 + x_M)$, and taking into account the expression (46) and the inequality (5) in the estimate of this contribution and the inequality (6) in the estimate of the contribution of capillary pressure to b_ν , we have in the region of partial dissolution of the nucleus the inequality

$$b_\nu < - \left(\frac{z_M + 1}{n_M + z_M} x_n + \frac{n_M - 1}{n_M + z_M} x_{cmc} \right) + \frac{2a_M}{3\nu_n^{1/3}} \quad (47)$$

where (as in (13), (28)) it is assumed for simplicity that the coefficient of proportionality between R_n and $\nu_n^{1/3}$ is approximately equal to the coefficient of proportionality between R_0 and $\nu_0^{1/3}$. Let us emphasize that the smallness of the overall concentration x , i.e., the inequality $x \ll 1$ in the region of partial dissolution of the nucleus, is not required for the applicability of the inequalities (6) and (47) in this region (although the smallness of the overall concentration x will in fact occur). The surface tension a of the drop in the region of partial dissolution of the nucleus may actually be somewhat smaller than a_M (since x_2 may be [7] appreciably greater than x_{cmc} — its highest value allowed approximately in [6]). This, however, will only strengthen the inequality (47).

According to (36), (47), the following will be sufficient to satisfy the condition (4):

$$x_n > \frac{2a_M (n_M + z_M)}{3 (z_M + 1) \nu_n^{1/3}} \left\{ 1 - \frac{[2a_M (n_M + z_M) + 3s_\infty (z_M + 1)]^{3/2}}{9a_M (z_M + 1)^{1/2} (n_M + z_M) \nu_n^{1/6}} \right\} \quad (48)$$

which imposes on the solubility x_n the desired limitation from below in the case of a micellar solution of ionic surfactants. Since the limitation (48) provides for the fulfillment of the condition (4) even when in (47) the inequality sign is replaced by an equality sign, it is evident from (2), (4), (11), (35), and (46) that the limitation (48) also guarantees the inequality (15).

The following approximate inequalities are clear from (41), (43):

$$\frac{2a_M (n_M + z_M)}{3 (z_M + 1) \nu_n^{1/3}} \leq 3 \left[\frac{(n_M + 3z_M) x_{cmc}}{2z_M} \right]^{2/3} \quad (49)$$

$$\frac{[2a_M (n_M + z_M) + 3s_\infty (z_M + 1)]^{3/2}}{9a_M (z_M + 1)^{1/2} (n_M + z_M) \nu_n^{1/6}} \leq \frac{2}{3} \left[\frac{(n_M + 3z_M) x_{cmc}}{2z_M} \right]^{1/3} \quad (50)$$

Along with (42), the inequalities (49), (50) show that the solution concentration specifying the lower bound of the limitation (48) on x_n decreases, and the limitation (48) itself correspondingly weakens as ν_n increases in the entire region of applicability of the theory developed in [6]. Moreover, along with (42), the inequality (50) shows that in the entire region of applicability of the theory developed in [6], the limitation (48) reduces to

$$x_n > \frac{2a_M (n_M + z_M)}{3 (z_M + 1) \nu_n^{1/3}} \quad (51)$$

and the inequality (49) also shows that at the limit of applicability of this theory, when the limitation (48) or (51) becomes the most stringent, it represents

$$x_n \geq 3 \left[\frac{(n_M + 3z_M) x_{cmc}}{2z_M} \right]^{2/3} \quad (52)$$

As is evident from (47), the limitation (51) is sufficient for the fulfillment of not only the condition (4), but also the stronger level $b_\nu < -(n_M - 1)x_{cmc}/(n_M + z_M)$ in the entire region of partial solution of the nucleus. According to (1), in this entire region, condensation will then take place without a barrier even when $b > -(n_M - 1)x_{cmc}/(n_M + z_M)$ (and not only when the inequality (3) is satisfied).

Since the quantity b_{tr} does not appear in the limitation (51) at all, the latter (in contrast to the limitation (48)) does not require the fulfillment of the inequality (39), which greatly narrows the interval of ν_n values that is allowed by the theory developed in [6] (in the region of complete dissolution of the nucleus, the solution can also be molecular).

For the limitation (51) to be applicable, the inequality (43) is sufficient. In fact, even when the overall concentration, which specifies the lower bound of the limitation (51), reaches the maximum value allowed by the inequality (43), equal to the value on the right side of the following conditions are (52), there are obeyed, as is clear from (46), (45) and from the strong inequalities $n_M \gg z_M \gg 1$, $x_{cmc} \ll 1$, and (42), the conditions

$$x_1 + x_2 + x_M \ll 1 \quad (53)$$

$$z_M^3 x_M \ll 1 \quad (54)$$

of diluteness of the solution in the drop and smallness in the latter of the electrical interaction of the micelles, these conditions having been assumed in the derivation of the limitation (51) (the condition (54) may possibly be obeyed at the limit). The fact that the maximum value of the overall concentration-itself determined by the value on the right side of (52)-which specifies the lower bound of the limitation (51), proves as a result of (42) to be very small compared to unity, qualitatively confirms the equality (37), which was also assumed in the derivation of the limitation (51) (a possible deviation from the equality (37), even in order of magnitude, is of no practical significance, as is evident from (33), (34), (42), and $n_M \gg z_M \gg 1$).

As has already been noted, for micellar solutions in which $n_M \gg 1$, the overall concentration x_n may be appreciable as compared to unity. According to (42), the maximum limitation (52) will then take place even with a large margin. Along with it, the limitation (51) for all ν_n at which the condition (43) of its applicability is satisfied will also take place with a large margin.

Discussion of results. When the solution of the substance of the nucleus is molecular (or ionic), and the substance of the nucleus can be both surface-inactive and surface-active, sufficient for a barrier-free condensation in the region of partial dissolution of the nucleus at all values of the chemical potential of the vapor at which the vapor is supersaturated ($b > 0$), the limitation (20) on the solubility x_n from below is valid. The condition (19) of applicability of this limitation is narrower than the condition (12) of applicability of the theory developed in [1] to the region of complete dissolution of the nucleus.

When the solution of the substance of the nucleus is micellar, and the substance of the nucleus is a nonionic colloidal surfactant, the limitation (29) on the solubility x_n from below is sufficient for a barrier-free condensation in the region of partial dissolution of the nucleus at all values of the chemical potential of the vapor at which condensation takes place without a barrier in the region of complete dissolution of the nucleus ($b \geq b_{tr}$). The condition (26) of applicability of this limitation is the same as the condition of applicability of the theory developed in [6] to the region of complete dissolution of the nucleus.

Finally, if the solution of the substance of the nucleus is micellar, and the substance of the nucleus is an ionic colloidal surfactant sufficient for a barrier-free condensation in the region of partial dissolution of the nucleus at all values of the chemical potential of the vapor at which the vapor is supersaturated or even slightly undersaturated ($b > - (n_M - 1) x_{cmc} / (n_M + z_M)$), the limitation (51) on the solubility x_n from below is valid. The condition (43) of applicability of this limitation, broader than the conditions of applicability of the theory developed in [6] to the region of complete dissolution of the nucleus — does not necessitate the additional condition (39) required for this theory.

In all the cases analyzed, which duplicate all the cases discussed in [1-6] in the region of complete dissolution of the nucleus, the conditions of applicability of the obtained limitation on x_n from below are acceptable in the case of such large sizes of condensation nuclei of greatest practical interest that condensation is possible at low vapor saturations.

For these sizes of condensation nuclei, the obtained limitation on x_n from below also becomes realistic, i.e., realizable in practice.

The above provides convincing evidence that at least when the sizes of the condensation nuclei are so large that condensation on them is possible at low vapor supersaturations, the region discussed in [1-6] of complete dissolution of the nuclei is important in finding the threshold value of the chemical potential of the vapor, which determines the threshold of barrier-free condensation in the entire range of variation of the number of condensate molecules, and not only in the region of complete dissolution of the nuclei.

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