THERMODYNAMICS OF CONDENSATION ON SOLUBLE SURFACTANT NUCLEI WITH VARIABLE ADSORPTION

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A complex pattern of behavior is observed by the extrema of the chemical potential of a substance condensed from vapor into a drop formed on a surfactant nucleus dissolved in the substance, with the adsorption of the surfactant on the drop surface being variable. The Langmuir and Shishkovsky formulas from the theory of monolayer surfactant adsorption are used to determine the adsorption of the surfactant from the nucleus and the surface tension of the drop as functions of the concentration of the solution inside the drop. It is shown that, depending on the values of the initial parameters of the size of the nucleus, there may be either one extremum (which will be maximal in this case) or three extrema (two of which must be maximum and one of which must be a minimum). A determination is made of the threshold value of the chemical potential of the vapor, which is determined by the maximum of the chemical potential of the condensate (or the larger of the maxima, in the case of two maxima). The results of the analytical theory are illustrated by direct numerical calculations of the chemical potential of the condensate as a function of the number of condensate molecules.

With allowance for the adsorption of the substance of the nucleus on the surface of a drop, the study [1] constructed a closed system of equations linking the thermodynamic characteristics of the drop when the chemical potential of the condensate has an extremum (here, the drop consists of condensate formed from the vapor phase). The present article is devoted to study of this system of equations in the general case of an arbitrary degree of saturation of monolayer adsorption.

The Langmuir and Shishkovsky formulas are used for the adsorption of the substance of the nucleus on the surface and the surface tension of the drop as functions of the concentration of the solution inside the drop. Widely used in the theory of the monolayer adsorption of surfactants, these formulas make it possible to fully explore the complex, nonlinear nature of the thermodynamics of condensation on soluble surfactant nuclei. Here, condensation thermodynamics are determined mainly by the degree of adsorption and the surface tension as functions of the concentration of the surfactant solution. Compared to the studies [1, 2] we focus on the cases of complete saturation of adsorption and a high degree of undersaturation.

Initial System of Equations. With allowance for adsorption, the closed system of equations constructed in [1] links the thermodynamic characteristics of a drop in which the condensate has a chemical-potential extremum:

$$(1 + 2u - 2u\,\partial \ln s / \partial \ln x)\,z^2 - 2\,(u + 3)\,z + 9 = 0, \tag{1}$$

$$u = v\,(\xi + 1)/\xi, \tag{2}$$

$$v = w - \ln(\xi + 1), \tag{3}$$

$$\partial \ln s / \partial \ln x = 1/(\xi + 1) \tag{4}$$

([1], Eqs. (40), (50-52)). Here:

$$z \equiv s\nu_0^{2/3}/\nu_n \quad (0 \leqslant z \leqslant 1), \tag{5}$$

$$u \equiv a/s, \tag{6}$$

$$\upsilon \equiv a/s_\infty, \tag{7}$$

$$w \equiv \bar{a}/s_\infty, \tag{8}$$

$$\xi \equiv x/x_\alpha \tag{9}$$

([1], definitions (32), (36), (46-48)). Henceforth: ν_0 is the total number of condensate molecules; ν_n is the total number of condensation-nucleus molecules or ions; x is the relative concentration of the substance of the nucleus in solution within the bulk phase of the drop; x_α is the characteristic (for the Langmuir and Shishkovsky formulas) value of concentration x such that filling of the surfactant adsorption monolayer begins at x $\ll$ x_α and is completed at x $\gg$ x_α (a quantitative definition of the characteristic value x_α is obtained from Eq. (13) in [1]); s is the dimensionless monolayer adsorption (determined by Eq. (4) in [1]); s_∞ is dimensionless monolayer adsorption for complete saturation of the monolayer); a is the dimensionless surface tension of the drop (determined by Eq. (4) from [3]); $\bar{a}$ is the dimensionless surface tension of the drop in the absence of adsorption. The quantities ν_n, xα, s_∞, and w are external parameters of the problem.

Together with definition (6), Eq. (1) expands into the thermodynamic equation

$$(\partial b_\nu/\partial \nu)_0 = 0, \tag{10}$$

where b_ν is the chemical potential of the condensate inside the bulk phase of the drop. The subscript zero characterizes the values of the quantities at the extremum of chemical potential (for simplicity, this subscript is indicated only for the quantity ν in (5-9)). Equations (2) and (4) follow from the Langmuir formula

$$s = s_\infty \xi/(\xi + 1) \tag{11}$$

([1], Eq. (49)), while Eq. (3) is equivalent to the Shishkovsky formula.

Following [1, 2] we choose the quantity z, defined by (5), as the independent variable to describe a drop for which the condensate has a chemical-potential extremum. The quantity z is the fraction of the total amount of the substance of the nucleus that is adsorbed. Here, the quantity ν_n (an external parameter of the problem) will be a function of z. As will be shown below, the variable z will also allow us to discern the entire thermodynamic pattern of behavior of the chemical-potential extrema of the condensate. No special problems are encountered in changing over in the final formulas from the independent variable z to the independent variable ν_n.

Concentration of the Solution Inside the Drop with an Arbitrary Degree of Monolayer Saturation. The following result is obtained from (1-2), (4) by elementary calculation

$$\frac{1}{\xi} = z - 1 + \frac{(3-z)^2}{2z\upsilon}. \tag{12}$$

Inserting (3) into (12), we obtain the equation

$$\frac{1}{\xi} = z - 1 + \frac{(3-z)^2}{2z\,|w - \ln(\xi + 1)|} \tag{13}$$

linking the variables z and ξ.

In accordance with (13), we have the asymptote

$$\xi = 2wz/9 \quad (z \ll 9/2w). \tag{14}$$

This asymptote ensures satisfaction of the inequality $\xi \ll 1$ in the region z $\ll$ 9/2 w in which it is valid.

Differentiating (12) with respect to z when w is fixed and using (3), we arrive at an equation for $\partial(1/\xi)/\partial z$. Solving this, we find

$$\frac{\partial(1/\xi)}{\partial z} = \frac{z^2(2\upsilon + 1) - 9}{2z^2\upsilon + z(3-z)^2\xi^2(\xi + 1)^{-1}\upsilon^{-1}}. \tag{15}$$
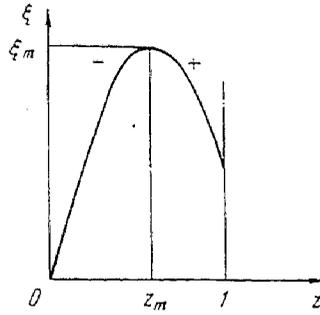
Fig. 1. Dependence of solution concentration ξ inside the drop on the variable z describing the drop.

The below relations follow from (15)

$$\partial\xi/\partial z > 0 \quad (z < z_m), \tag{16}$$

$$\partial\xi/\partial z = 0 \quad (z = z_m), \tag{17}$$

$$\partial\xi/\partial z < 0 \quad (z > z_m), \tag{18}$$

where the value of z_m yielding the maximum of the concentration ξ of the solution inside the drop with the chemical-potential extremum of the condensate satisfies the equation

$$z_m = \frac{3}{(2v_m + 1)^{1/2}}. \tag{19}$$

the subscript m denotes values of quantities at the point $z = z_m$, where concentration ξ is maximal (at the extremum of condensate chemical potential). In accordance with (12), for the maximum value of ξ_m the concentration ξ:

$$\frac{1}{\xi_m} = z_m - 1 + \frac{(3 - z_m)^2}{2 z_m v_m}. \tag{20}$$

In accordance with (3), the greater ξ, the smaller v. The value v_m is thus the minimum value for v. It should be noted that the general information presented above on the concentration ξ of the solution inside the drop was obtained without solving Eq. (13) for ξ (which is impossible to do analytically).

Relations (16-18) are analogous to relations (9-11) in [2] for a model of a drop with a constant degree of adsorption. However, the value of z_m is now different, while the derivative $\partial\xi/\partial z$ — as shown by asymptote (14) — tends toward a finite nontrivial value as $z \to 0$. At the same time, concentration ξ also approaches a finite nontrivial value as $z \to 1$. In fact, we find from (12) that

$$\xi|_{z=1} = (v/2)|_{z=1}. \tag{21}$$

In accordance with (21), we may even obtain $\xi|_{z=1} \gg 1$. Although the condition $\xi \gg 1$ for the validity of the drop model with constant adsorption is satisfied in this case, Eq. (21) nevertheless yields results which diverge from those obtained from nucleation theory in the given model — in which $\xi = 0$ at $z = 1$ [2]. The reason for the difference lies in the fact that in the drop model with constant adsorption (in which $s = s_\infty$) attainment of the limiting value $z = 1$ is only a formal possibility. Specifically, it is possible only at the value $(v_n/s_\infty)^{3/2}$ of the variable z at which $\xi = 0$, in accordance with the equation of the material balance in the drop

$$x = v_n v^{-1} - s v^{-1/3} \tag{22}$$

([1], Eq. (5)) and definition (9). In the theory which considers the dependence of adsorption on solution concentration inside the drop, attainment of the limiting value $z = 1$ is actually possible (albeit asymptotically). This occurs with the natural inequality $\xi > 0$ remaining in force.

It was also noted in [2] that the nucleation theory in the drop model with constant adsorption becomes invalid as the variable z approaches its upper limit $z = 1$.

Figure 1 shows the behavior of concentration ξ in relation to z as determined from (16-18), (14), and (21).

Thermodynamics of a Drop with an Arbitrary Degree of Monolayer Saturation. In accordance with general thermodynamic expressions (34-35) from [1], we obtain the following with allowance for Eq. (11) and definition (9):

$$\nu_n^{1/2} = \frac{s_\infty^{3/2}}{x_\alpha} \frac{1-z}{z^{3/2}} \frac{\xi^{1/2}}{(\xi+1)^{3/2}} ,$$ (23)

$$\nu_0^{1/3} = \frac{s_\infty}{x_\alpha} \frac{1-z}{z} \frac{1}{\xi+1} .$$ (24)

Equations (23), (24) become the analogous expressions (17-18) from [2] in the case $\xi \gg 1$, although the dependence of ξ on z may even then (with $\xi \gg 1$) be the same as in the drop model with constant adsorption.

In the other limiting case, $\xi \ll 1$, we have the following in accordance with (14), (23-24):

$$\nu_n^{1/2} = \frac{s_\infty^{1/2}}{x_\alpha} \frac{(2w)^{1/2}}{3z} \quad (z \ll 9/2w),$$ (25)

$$\nu_0^{1/3} = (9\nu_n/2\,\overline{a})^{1/2} \quad (z \ll 9/2w),$$ (26)

where the quantity $1 - z$ is identified with 1 (at $z \ll 9/2w$). Asymptote (26) corresponds to Eq. (25) from [1] for the case of a high degree of undersaturation of adsorption. Expressing z in the above-obtained asymptote (14) in terms of $\nu_n^{1/2}$ by means of (25) and considering (8-9), we also find that (14) corresponds to Eq. (26) from [1] for the case of a high degree of adsorption undersaturation.

We use (23-24) to obtain the relations

$$\nu_n^{1/2}\big|_{z=1} = 0,$$ (27)

$$\nu_0^{1/3}\big|_{z=1} = 0.$$ (28)

Since these relations ensure a drop volume equal to zero, they are consistent with Eq. (21). In accordance with the latter, solution concentration at $z = 1$ differs from 0. Drop volume decreases more rapidly than the area of its surface as the size of the drop approaches 0. It is understood that (27-28) have a purely formal meaning in the macroscopic theory.

We can use (23) to find

$$\frac{\partial \nu_n^{1/2}}{\partial z} = \frac{s_\infty^{3/2}}{2x_\alpha} \left\{ \frac{1-z}{z^{3/2}} \frac{\xi^{1/2}(2\xi-1)}{(\xi+1)^{5/2}} \frac{\partial(1/\xi)}{\partial z} - \frac{(3-z)}{z^{5/2}} \frac{\xi^{1/2}}{(\xi+1)^{3/2}} \right\}$$ (29)

Partial derivatives are taken with fixed parameters x_α, s_∞, and w. The second term in the right side of (29) is negative throughout the physical region $0 \le z \le 1$.

However, as is clear from (16), the first term in the right side of (29) will also be negative in any region in which $\xi > 1/2$ and $z < z_m$. Thus, in accordance with (29), $\partial \nu_n/\partial z < 0$ throughout this region — including the very point $z = z_m$ at which (following (17), (29)) the below equation is valid

$$\frac{\partial \nu_n^{1/2}}{\partial z}\bigg|_{z=z_m} = -\frac{s_\infty^{3/2}}{2x_\alpha} \frac{3-z_m}{z_m^{5/2}} \frac{\xi_m^{1/2}}{(\xi_m+1)^{3/2}}$$ (30)

Asymptote (25) shows that the inequality $\partial \nu_n/\partial z < 0$ is also valid at $z \ll 9/2w$, when $\xi \ll 1$. Thus, it is certain that the condition $\xi > 1/2$ is violated. Although the first term in the right side of (29) remains positive in this case, it is less than the absolute value of the second (negative) term in the right side of (29). Thus, the inequality $\partial \nu_n/\partial z < 0$ holds throughout the region $0 \le z \le z_m$.

Generally speaking, it is impossible to definitively establish the sign of the derivative $\partial\nu_n^{1/2}/\partial z$ in the region $z_m < z \leq 1$. However, it can be determined that the derivative $\partial\nu_n^{1/2}/\partial z$ is nonetheless negative at the upper boundary $z = 1$ of this region. In fact, in accordance with (21), (29), we have

$$\frac{\partial\nu_n^{1/2}}{\partial z}\Bigg|_{z=1} = -\frac{s_\infty^{1/2}}{x_\alpha}\frac{\nu^{1/2}}{(\nu+2)^{1/2}}\Bigg|_{z=1} \tag{31}$$

If the parameter w is large enough so that the inequality

$$\exp(w - 12) \gg 1 \tag{32}$$

is observed, (this inequality being necessary in the constant-adsorption drop model so that the chemical-potential extremum of the condensate can be obtained with complete saturation of the adsorption monolayer — see inequality (14) in [2]), then the derivative $\partial\nu_n^{1/2}/\partial z$ changes twice within the region $z_m < z \leq 1$. This will become clear from the subsequent discussion. Since, in accordance with (30), this derivative is negative at $z = z_m$, it becomes positive with an increase in the variable z from the value $z = z_m$ and then again becomes negative — in accordance with (31) — as z approaches $z = 1$.

Consequently, by turning out to be a necessary condition in the drop model with constant adsorption, inequality (32) illustrates an important fact in the general theory of nucleation with variable adsorption: The derivative $\partial\nu_n^{1/2}/\partial z$ is not negative anywhere within the physical region $0 \leq z \leq 1$ of the variable z. As is clear from (8) satisfaction of inequality (32) in fact requires that surface tension α be fairly high in the absence of adsorption and, conversely, that adsorption s_∞ be fairly small with complete saturation of the monolayer.

Further progress in the thermodynamics of nucleation with an arbitrary degree of monolayer saturation is impossible without solving Eq. (13), linking the variables z and ξ. In turn, as already noted, Eq. (13) cannot be solved for the variable ξ in analytical form (in contrast to the analogous equation in the drop model with constant adsorption).

Concentration of Surfactant Solution Inside the Drop as a Variable in the Description of the Drop. Equation (13), connecting the variables z and ξ, can be solved for z. We will take advantage of this property of Eq. (13) below (the equation is necessarily quadratic due to the form of general thermodynamic equation (1) in the variable z).

Accordingly, instead of z, we take the solution concentration ξ inside the drop as the independent variable to describe the drop (in which the condensate has a chemical potential with an extremum). No particular difficulties are encountered in changing over in the final formulas from the independent variable ξ to the more convenient (for analyzing the results) independent variable z and then changing from z to the natural (for practical purposes) variable ν_n.

Thus, choosing concentration ξ as the independent variable and solving Eq. (13) for z, we obtain

$$z_{\mp} = \frac{(\xi+1)\nu + 3\xi \mp \sqrt{(\xi+1)^2\nu^2 - 6\xi(2\xi-1)\nu}}{\xi(2\nu+1)} \tag{33}$$

The superscripts $-$ and $+$ with the variable z denote the two branches of its dependence on ξ (these branches correspond to the minus sign and plus sign next to the curve in Fig. 1). In accordance with (3), the quantity v is in turn a function of ξ with fixed x_α, s_∞, and w. We can use (33) to also find the inverse dependence of ξ on z. This will be done below.

Together with the formulas obtained above, Eq. (33) gives an analytical solution for the entire nonlinear problem of finding the thermodynamic characteristics of a drop having a chemical-potential extremum with an arbitrary degree of saturation of the monolayer of the nucleus substance on the drop surface.

With allowance for (3) it follows from (33) that

$$z_- = 9\xi/2w \quad (\xi \ll 1) \tag{34}$$

Comparing (34) and (14), we see that the branch z_- of the dependence of z on ξ in Eq. (33) includes an asymptotic part corresponding to a high degree of undersaturation of monolayer adsorption.

The fact that Eq. (33) is real-valued implies satisfaction of the condition

$$\nu \geq \frac{6\xi(2\xi-1)}{(\xi+1)^2} \tag{35}$$

The two branches z_- and z_+ of the dependence of z on ξ in Eq. (33) merge at the point $\xi = \xi_m$, $z = z_m$ (see Fig. 1). The quantity under the square root sign in (33) vanishes at this point, while (35) becomes

$$v_m = \frac{6\xi_m (2\xi_m - 1)}{(\xi_m + 1)^2} \tag{36}$$

As is clear from (3), a decrease in concentration ξ from its maximum value ξ_m is accompanied by a monotonic increase in the quantity in the left side of (35) from its minimum v_m. Here, the quantity in the right side of (35) decreases monotonically. However, the inequality $\xi > 1/5$ remains valid. Before this inequality is violated, the quantity in the right side of (35) becomes negative (at $\xi > 1/2$). This ensures satisfaction of condition (35).

In sum, it is apparent that Eq. (36) guarantees satisfaction of limitation (35). The equality sign exists in (35) only when $\xi = \xi_m$. If $\xi < \xi_m$, there will be an inequality sign in (35). It is also evident from (36) that we will always at least have $\xi_m \geq 1/2$ and $v_m \leq 12$.

Solving Eq. (36) for ξ_m, we obtain

$$\xi_m = \frac{v_m}{3(2v_m + 1)^{1/2} - v_m - 3} \tag{37}$$

In accordance with (20) and (37), we obtain the previous relation (19).

The below formula follows from Eqs. (19) and (36)

$$z_m = \frac{3(\xi_m + 1)}{5\xi_m - 1} \tag{38}$$

this formula expressing z_m directly through the maximum concentration ξ_m. Also following from (19) and (36) is the inverse of (38)

$$\xi_m = \frac{z_m + 3}{5z_m - 3} \tag{39}$$

Expanding (36) in accordance with (3), we arrive at a closed equation for ξ_m:

$$w - \ln(\xi_m + 1) = \frac{6\xi_m (2\xi_m - 1)}{(\xi_m + 1)^2} \tag{40}$$

It is clear from the above proof of condition (35) by means of Eq. (36) that the root ξ_m of Eq. (40) is unique (for each assigned w).

If the inequality $\xi_m \gg 1$ is satisfied, then it can be concluded with a high degree of accuracy that the quantities in the right sides of (36) and (40) will have a value of 12. With a similarly high degree of accuracy, it then follows from (36) and (40) that

$$v_m = 12 \tag{41}$$
$$\xi_m = \exp(w - 12) \tag{42}$$

while it follows from (19) that

$$z_m = 3/5 \tag{43}$$

It turns out that 12 is the maximum possible value of v_m in the general case. With $\xi_m \gg 1$, Eq. (43) is easily found directly by means of (38). In addition, (38) can easily be used to determine that 3/5 is in general the minimum possible value for z_m. It is also apparent from (40) that the inequality $\xi_m \gg 1$ holds when inequality (32) is observed (the latter inequality is not fundamental to the general theory of condensation with arbitrary adsorption). Equations (41-43) agree with relations (14), (13), and (12), respectively, in [2] for the drop model with constant adsorption.

Taking (15) into account and using (42-43), we can show that the following relation is valid when inequality (32) is satisfied
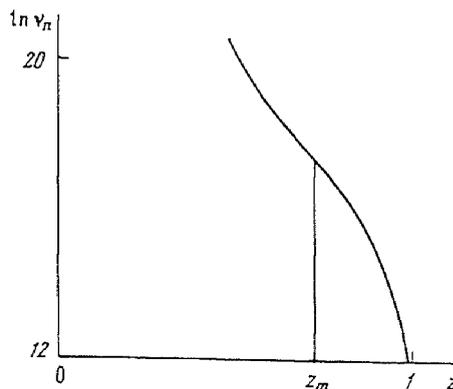
Fig. 2. Dependence of $\ln v_n$ on z with $w = 10$, $x_\alpha = 10^{-5}$, and $s_\infty = 1$.
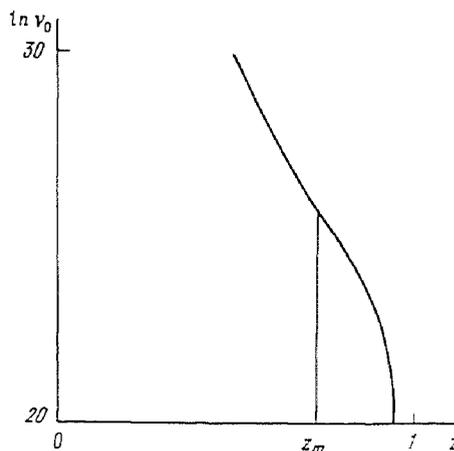
Fig. 3. Dependence of $\ln v_0$ on z with $w = 10$, $x_\alpha = 10^{-5}$, and $s_\infty = 1$.

$$(\partial^2 \xi / \partial z^2)|_{z = z_m} = -(625/6)\xi_m \tag{44}$$

this relation coinciding with Eq. (16) from [2]. Together with (17), (42), and (43), Eq. (44) shows that the dependence of concentration ξ on the variable z in the neighborhood of the point $z = z_m$ of the concentration maximum and the position of this point on the z axis are the same with satisfaction of inequality (32) in the nucleation theory in which adsorption is constant and in the nucleation theory in which allowance is made for the concentration dependence of adsorption. This should be expected, since, in the neighborhood of the point $z = z_m$, the condition $\xi \gg 1$ of validity of the drop model with constant adsorption is always satisfied with inequality (32).

In accordance with (41), the value of v found from (7) for the maximum solution concentration inside the drop has the same minimum $v_m = 12$ whether or not inequality (32) is satisfied. This confirms the conclusion reached in regard to the constant-adsorption model in [2]: the solution concentration inside the drop - where chemical potential has an extremum - has a stabilizing effect on the minimum value of the surface tension of the drop.

If (32) is violated, then $v_m < 12$ (and $z_m > 3/5$). As has already been noted, the value 12 is the maximum value possible for v_m (even though v_m is itself the minimum value of v for each assigned w).

Extrema of Condensate Chemical Potential with Arbitrary Monolayer Saturation. Let us discuss the results calculated on the basis of exact formulas (23-24), (29), (33), (36), (38), and (40) of the nucleation theory in which allowance is made for the dependence of adsorption on the drop surface on the concentration of the solution inside the drop.

We begin with the situation in which inequality (32) — equivalent to the inequality $\xi_m \gg 1$ — is violated. We set $w = 10$. Solving Eq. (40) for ξ_m in this case, we obtain $\xi_m = 5.96$. In accordance with (36) and (38), we then have $v_m = 8.06$ and $z_m = 0.725$.

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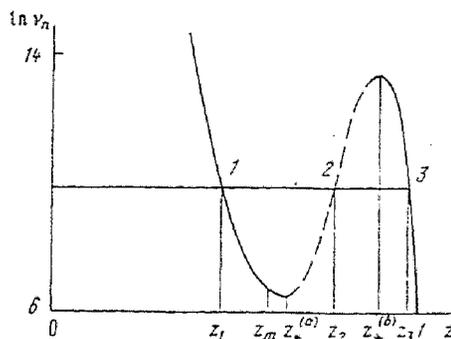
Fig. 4. Dependence of ln ν_n on z with w = 20, $x_\alpha = 10^{-5}$, and $s_\infty = 1$.

Figure 2 shows the dependence of ν_n on the variable z in its physical region $0 \leq z \leq 1$ for w = 10. This curve was constructed from (23), (29), (33) and is shown in logarithmic scale. We put $x_\alpha = 10^{-5}$ and $s_\infty = 1$.

It is apparent that ν_n decreases monotonically with an increase in z throughout the region $0 \leq z \leq 1$. In accordance with (25), this decrease begins from the asymptotic value ∞ as z = 0 and, in keeping with (27), (31), approaches 0 as z → 1.

Thus, for each assigned ν_n within the interval $0 < \nu_n < \infty$, there is only one extremum for the chemical potential of the condensate. Of course, this extremum will be a maximum (as is clear from the general hypothesis that the chemical potential of the condensate approaches $-\infty$ as $\nu \to 0$).

Figure 3 also uses a logarithmic scale to show the dependence of ν_0 on z in its physical region $0 \leq z \leq 1$ at w = 10. This dependence was obtained from (24), (33). A qualitative indication of the value $z_m = 0.0725$ is given relative to the z axis. We put $x_\alpha = 10^{-5}$ and $s_\infty = 1$.

It is apparent that ν_0 decreases monotonically with an increase in z throughout the region $0 \leq z \leq 1$. This decrease begins from the asymptotic value ∞ at z = 0 (in accordance with (25-26)) and approaches 0 as z → 1 (in accordance with (28)).

Let us now turn to the opposite situation, in which inequality (32) — equivalent to the inequality $\xi_m >> 1$ — is observed. In this case, Eqs. (41-43) will also be valid. We put w = 20. In accordance with (42), we then have $\xi_m = 3 \cdot 10^3$.

Figure 4 uses the logarithmic scale to show the dependence of ν_n on the variable z in its physical region $0 \leq z \leq 1$ at w = 20. This dependence was constructed from (23), (29), (33). A qualitative indication is given of the value $z_m = 0.6003$ on the z axis. We put $x_\alpha = 10^{-5}$, $s_\infty = 1$.

As before, the curve of the dependence of ν_n on z agrees with (25), (27), (31). However, the quantity ν_n no longer decreases monotonically with z. It is apparent that

$$\partial \nu_n / \partial z < 0 \qquad (z < z_*^{(a)}) \tag{45}$$

$$\partial \nu_n / \partial z = 0 \qquad (z = z_*^{(a)}) \tag{46}$$

$$\partial \nu_n / \partial z > 0 \qquad (z_*^{(a)} < z < z_*^{(b)}) \tag{47}$$

$$\partial \nu_n / \partial z = 0 \qquad (z = z_*^{(b)}) \tag{48}$$

$$\partial \nu_n / \partial z < 0 \qquad (z > z_*^{(b)}) \tag{49}$$

where $z_*^{(a)}$ and $z_*^{(b)}$ are coordinates of points at which ν_n reaches a minimum and a maximum on the z axis, respectively. When w = 20, $x_\alpha = 10^{-5}$, $s_\infty = 1$, we have $z_*^{(a)} = 0.645$, $z_*^{(b)} = 0.905$, $\nu_{n*}^{(a)} = 645$, $\nu_{n*}^{(b)} = 2.5 \cdot 10^5$, where $\nu_{n*}^{(a)}$ and $\nu_{n*}^{(b)}$ are the values of the minimum and maximum for ν_n. The following is valid

$$z_m < z_*^{(a)} < z_*^{(b)} \tag{50}$$

so that at $0 \leq z \leq z_m$ we always have $\partial \nu_n / \partial z < 0$. Also naturally valid is the expression

$$\nu_{n*}^{(a)} < \nu_{n*}^{(b)} \tag{51}$$

Thus, we now have three basic possibilities for each assigned value of ν_n within the interval $0 < \nu_n < \infty$.

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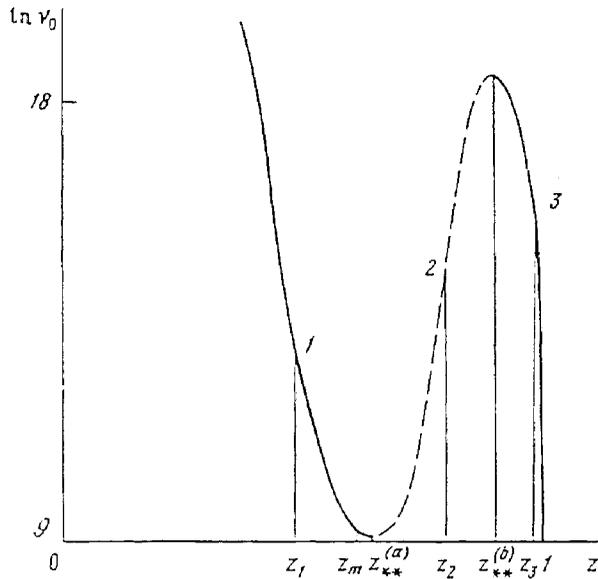
Fig. 5. Dependence of $\ln \nu_0$ on z with w = 20, $x_\alpha =$ 10^{-5}, and $s_\infty = 1$.

If $0 < \nu_n < \nu_{n*}^{(a)}$, then chemical potential b_ν has only one extremum. This extremum will be a maximum.

If $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$, then chemical potential will have three extrema. Two of these will be maxima and one will be a minimum. In this case

$$z_1 < z_*^{(a)}, \; z_*^{(a)} < z_2 < z_*^{(b)}, \; z_3 > z_*^{(b)} \tag{52}$$

where the values z_1 and z_3 of the variable z characterize drops having maxima of chemical potential b_ν. The value z_2 of the variable z characterizes a drop having a minimum of chemical potential b_ν.

Finally, if $\nu_n > \nu_{n*}^{(b)}$, then chemical potential b_ν will again have only one extremum. This will be a maximum.

The part of the curve of the dependence of ν_n on z shown in Fig. 4 by the solid line for $0 \le z \le z_*^{(a)}$ and $z_*^{(b)} \le z \le 1$ corresponds to a maximum of chemical potential b_ν, while the part of this curve shown by the dashed line for $z_*^{(a)} < z < z_*^{(b)}$ corresponds to a minimum of chemical potential b_ν. Points 1 and 3 on the curve correspond to drops which have a maximum of chemical potential b_ν for the assigned ν_n. Point 2 on the curve corresponds to a drop which, for the assigned ν_n, has a minimum of chemical potential b_ν.

Figure 5 uses the logarithmic scale to present the curve of the dependence of ν_0 on the variable z within its physical region $0 \le z \le 1$ at w = 20. This curve was constructed from (24), (33). We put $x_\alpha = 10^{-5}, s_\infty = 1$. For the coordinates $z_{**}^{(a)}$ and $z_{**}^{(b)}$ on the z axis — at which ν_0 reaches a minimum and a maximum, respectively — we have (with w = 20) $z_{**}^{(a)} = 0.643$ and $z_{**}^{(b)} = 0.904$. The parts of the dependence of ν_0 on z shown by the solid and dashed lines in Fig. 5 have the same significance as in Fig. 4. This is also true of points 1-3 on the curve. These points correspond to values of $\nu_{01}, \nu_{02},$ and ν_{03} — roots of Eq. (10). The curve agrees with (25-26), (28).

Let us see how the values $\nu_{01}, \nu_{02},$ and ν_{03} are positioned on the axis of the variable ν relative to each other for the assigned ν_n. Here, we have

$$\nu_{n1}^{1/2} = \nu_{n2}^{1/2} = \nu_{n3}^{1/2} \tag{53}$$

It follows from (23-24) that

$$\nu_0^{1/2}/\nu_n^{1/2} = z^{-1/2}(\xi + 1)^{1/2} \xi^{1/2} s_\infty^{1/2} \tag{54}$$

In accordance with (17-18), we have

$$\partial [z (\xi + 1)/\xi]/\partial z > 0 \quad (z \geqslant z_m) \tag{55}$$

(the range of application of this inequality is actually broader than indicated). By virtue of (50) and (52), we find that

$$z_m < z_2 < z_3 \tag{56}$$

Using (53-56), we obtain

$$\nu_{02} < \nu_{03} \tag{57}$$

Thus, with the assigned ν_n, the value of ν_{02} ensuring a minimum of chemical potential b_ν is to the left of ν_{03} (which ensures a maximum of chemical potential b_ν) on the axis of the variable ν.

Since the minimum is located between two maxima, it also follows from (57) that

$$\nu_{01} < \nu_{02} < \nu_{03} \tag{58}$$

This additionally shows the relative location of ν_{01}, ν_{02}, and ν_{03} on the ν axis for an assigned ν_n. It is obvious that (58) is consistent with the general hypothesis that the chemical potential of the condensate approaches $-\infty$ as $\nu \to 0$ and ceases to depend on ν when $\nu \to \infty$.

Region of Coexistence of Three Chemical-Potential Extrema. As has already been noted, with an increase in the parameter w, the monotonic decrease in ν_n with an increase in z is replaced by a nonmonotonic decrease in ν_n. Let us determine the values of w at which this change takes place.

Regarding Eqs. (46) and (48) as the equations for the coordinates $z_*^{(a)}$ and $z_*^{(b)}$ of the minimum and maximum of the dependence of ν_n on z, we write these equations as follows with the use of (29), (15), and (12)

$$f(z)|_{z=z_*^{(a)}} = 0, \quad f(z)|_{z=z_*^{(b)}} = 0 \tag{59}$$

where

$$f(z) = 1 - z - \frac{(3-z)(3-2z)}{2zv} - \frac{(3-z)^2}{4z^3v^2}(z^2 - z + 3) \tag{60}$$

Together with the function f(z), we will also need its derivative f'(z) with respect to z. In accordance with (60), (9), (15), and (12), we have

$$f'(z) = \frac{1}{4z^4v^2} \left\{ -z^4(2v+1)^2 + 18z^2(v+1) - 54z + 81 + \right.$$

$$\left. \frac{4z(3-z)[z^2(3-2z)v + (3-z)(z^2-z+3)][z^2(2v+1)-9]}{[2z(z-1)v + (3-z)^2][2z^2v + (3-z)^2] + 2z(3-z)^2} \right\} \tag{61}$$

Taking $z_*^{(a)}$ and $z_*^{(b)}$ as assigned values, we can use (59-60) to obtain a quadratic equation for v at the points $z = z_*^{(a)}$ and $z = z_*^{(b)}$. Solving this equation, we obtain

$$v = \frac{3-z}{4z^2(1-z)}[z(3-2z) + \sqrt{z(12 - 7z - 4z^2)}] \quad (z = z_*^{(a)} \text{ и } z = z_*^{(b)}) \tag{62}$$

The second root of the equation is negative and is thus of no physical interest.

The replacement of the monotonic decrease in ν_n with an increase in z by a nonmonotonic decrease in the former occurs when the parameter w reaches the boundary value w_b at which

$$z_*^{(a)} = z_*^{(b)} = z_b \tag{63}$$

Here, the coordinates $z_*^{(a)}$ and $z_*^{(b)}$ of the minimum and maximum of $\nu_n(z)$ join to give the coordinate z_b of the point of inflection. It follows from (59), (63) that

$$f(z)|_{z=z_b} = 0 \tag{64}$$

$$f'(z)|_{z=z_b} = 0 \tag{65}$$

Equation (64) is equivalent to the equation obtained from (62) with observance of (63) for v at the point $z = z_b$. Inserting (63) into Eq. (65) after expansion of the latter by means of (61) yields a closed algebraic equation for the sought quantity z_b. The equation contains no external parameters and has a single positive real root.

Solving the equation numerically, we find

$$z_b = 0.757 \tag{66}$$

In accordance with (62), (66), and (12), the values v_b and ξ_b corresponding to v and ξ for the point of inflection $z = z_b$ are:

$$v_b = 11.89, \quad \xi_b = 27.35 \tag{67}$$

Finally, using (67) and (3), we obtain

$$w_b = 15.23 \tag{68}$$

The values of v_b, ξ_b, and w_b - as z_b itself - are independent of the external parameters.

In essence, the conditions $w < w_b$ and $w > w_b$ distinguish the two characteristic situations examined above. Relation (68) makes it possible to accurately determine which of the situations prevails in reality. Previously, we could have made such a judgment only on the basis of whether or not strong inequality (32) was observed.

Besides satisfaction of the condition $w > w_b$, the simultaneous existence of three chemical-potential extrema implies satisfaction of the condition $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$. Thus, we must find $\nu_{n*}^{(a)}$ and $\nu_{n*}^{(b)}$ in order to determine the region in which these three extrema coexist.

First we find $z_*^{(a)}$ and $z_*^{(b)}$. The value of $z_*^{(a)}$ is close to z_m. Thus, the following is valid with a high degree of accuracy

$$f(z_m^{(a)}) \simeq f(z_m) + f'(z_m) \cdot (z_*^{(a)} - z_m) \tag{69}$$

Considering the equality that follows from (36) and (39)

$$v_m = \frac{9 - z_m^2}{2z_m^2} \tag{70}$$

we find on the basis of (60-61) that

$$f(z_m) = -\frac{z_m^2 + 16z_m - 9}{(3 + z_m)^2} \tag{71}$$

$$f'(z_m) = \frac{9}{(3 + z_m)^2} \tag{72}$$

Inserting (71-72) into (69) and then taking (59) into account, we arrive at an equation for $z_*^{(a)}$. Solving this equation, we find

$$z_*^{(a)} \simeq \frac{1}{9} (z_m^2 + 25z_m - 9) \tag{73}$$

The value of $z_*^{(b)}$ is close to 1. Thus, the following expression is valid with a high degree of accuracy

$$f(z_*^{(b)}) \simeq f(1) + f'(1)(z_*^{(b)} - 1) \tag{74}$$

Proceeding on the basis of (60-61), we have

$$f(1) = -\frac{v+3}{v^2}\bigg|_{z=1}$$

(75)

$$f'(1) = -\frac{2v^3 - 2v^2 - 45v - 42}{2v^2(v+3)}\bigg|_{z=1}$$

(76)

Inserting (75-76) into (74) and then considering (59), we arrive at an equation for $z_*^{(b)}$. Solving this equation, we find

$$z_*^{(b)} \simeq \frac{2v^3 - 4v^2 - 57v - 60}{2v^3 - 2v^2 - 45v - 42}\bigg|_{z=1}$$

(77)

The quantities z_m and $v \mid_{z=1}$ in Eqs. (73) and (77) are unambiguously related to the parameter w by relations that follow from (39-40) and (21), (3), respectively

$$w = \frac{9 - z_m^2}{2z_m^2} + \ln\left(\frac{6z_m}{5z_m - 3}\right)$$

(78)

$$w = v\mid_{z=1} + \ln\left(\frac{v+2}{2}\right)\bigg|_{z=1}$$

(79)

In accordance with (78-79) we have $z_m = 0.6003$ and $v \mid_{z=1} = 17.7$ at $w = 20$. Using Eqs. (73) and (77), we then find: $z_*^{(a)} = 0.64$ (exact value $z_*^{(a)} = 0.645$) and $z_*^{(b)} = 0.91$ (exact value $z_*^{(b)} = 0.905$). Further, when $w = w_b = 15.23$, we have: $z_m = 0.6156$, $v \mid_{z=1} = 13.2$. Using formulas (73) and (77), we then find: $z_*^{(a)} = 0.75$ and $z_*^{(b)} = 0.85$ (by virtue of (63) and (66), the exact values would be $z_*^{(a)} = z_*^{(b)} = z_b = 0.757$).

It is apparent that Eq. (73) ensures a high degree of accuracy for all $w > w_b$. The accuracy of formula (77) is lower only when w is slightly greater than w_b.

Together with formulas (62) and (3), formulas (23) and (73) give a closed expression for $\nu_{n*}^{(a)}$ for assigned values of x_α, s_∞, and w. Similarly, together with formulas (62) and (12), formulas (23) and (77) give a closed expression for $\nu_{n*}^{(b)}$ with assigned x_α, s_∞, and w.

Threshold Value of the Chemical Potential of the Vapor in Nucleation on Nuclei of Soluble Surfactants. In accordance with general thermodynamic formula (41) from [1] the following is valid for the extreme value $(b_\nu)_0$ of the chemical potential of the condensate b_ν

$$(b_\nu)_0 = x\left[\frac{2zu}{3(1-z)} - 1\right]$$

(80)

The chemical potential of the condensate b_ν is expressed in thermal units of energy and is reckoned from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planer.

The threshold value b_{tr} of the chemical potential of the vapor is determined by the maximum of the chemical potential of the condensate b_ν or — if there is more than one maximum — by the largest of the maxima. We express the threshold value b_{tr} (as b_ν) in thermal energy units and reckon it from the value corresponding to equilibrium of the vapor with the condensing liquid when their contact surface is planer.

When allowance is made for the effect of the concentration of the solution inside a drop on the degree of adsorption of the surfactant on the drop surface, we find that there are two characteristic situations in regard to the thermodynamics of condensation on soluble surfactant nuclei.

First we will examine the situation in which inequality (32) is not satisfied (more exactly, when $w < w_b$). In this case, Eq. (10) will have one root ν_0 within the interval $0 < \nu_n < \infty$ for each assigned ν_n. It yields a maximum of chemical potential b_ν. Accordingly, when

$$b_{tr} = (b_\nu)_0$$

(81)

where, in accordance with (80), (2), and (9):

$$(b_\nu)_0 = x_\alpha \xi\left[\frac{2z(\xi+1)v}{3(1-z)\xi} - 1\right]$$

(82)

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Now we will examine the second situation, when, conversely, inequality (32) is observed (more exactly, when $w > w_b$).

If the value of the parameter ν_n turns out to be within the interval $0 < \nu_n < \nu_{n*}^{(a)}$ or the interval $\nu_n > \nu_{n*}^{(b)}$, then Eq. (10) has one root ν_0. It gives a maximum of chemical potential b_ν. In this case, Eqs. (81) and (82) remain valid (although the values of z, ξ, and v in these expressions will be different, of course).

If the value of ν_n turns out to lie within the interval $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$, then Eq. (10) has two roots $\nu_0 = \nu_{01}$ and $\nu_0 = \nu_{03}$. These roots give a maximum of chemical potential b_ν (there is also another root, $\nu_0 = \nu_{02}$, which gives a minimum of chemical potential b_ν). Since the threshold chemical potential of the vapor is determined by the larger of the maxima of chemical potential b_ν, then

$$b_{tr} = \max\ [(b_\nu)_{01}, (b_\nu)_{03}] \tag{83}$$

where, in accordance with (80), (2), and (9):

$$(b_\nu)_{0i} = x_\alpha \xi_i \left[\frac{2 z_i\ (\xi_i + 1)\ v_i}{3\ (1 - z_i)\ \xi_i} - 1 \right] \tag{84}$$

(ξ_i, v_i correspond to values z_i of the variable z; $i = 1, 3$). When $i = 2$, Eq. (84) determines the minimum of chemical potential b_ν.

Previous sections of this article described algorithms for finding the quantities in the right sides of (82) and (84) with assigned external parameters ν_n, x_α, s_∞, and w.

In place of (81) and (83), we can easily find a single expression for the threshold value b_{tr} of the chemical potential of the vapor when inequality (32) is satisfied (more exactly when $w > w_b$). We will use the subscript 3 to denote the single root ν_0 of Eq. (10) at $0 < \nu_n < \nu_{n*}^{(a)}$ and the corresponding values of z, ξ, v, and $(b_\nu)_0$. This number will at the same time serve to emphasize that the given root is an analytic continuation of the root ν_{03} from the region $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$. In addition, we will use the subscript 1 to denote the single root ν_0 of Eq. (10) at $\nu_n > \nu_{n*}^{(b)}$ and the corresponding values of z, ξ, v, and $(b_\nu)_0$. This number also serves to emphasize that the given root is an analytic continuation of the root ν_{01} from the region $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$. Then combining (81) and (83), we obtain

$$b_{tr} = \begin{cases} (b_\nu)_{03} & (0 < \nu_n < \nu_{n*}^{(a)}) \\ \max\ [(b_\nu)_{01}, (b_\nu)_{03}] & (\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}) \\ (b_\nu)_{01} & (\nu_n > \nu_{n*}^{(b)}) \end{cases} \tag{85}$$

where $(b_\nu)_{0i}$ is determined from Eq. (84).

In the case of a high degree of undersaturation of the monolayer on the drop surface — when Eq. (10) has one root (corresponding to a maximum of chemical potential b_ν) — we can use (80), (2-3), and (14) to obtain the simple asymptotic expression

$$b_{tr} = 2x = 2x_\alpha \xi \quad (\xi \ll 1) \tag{86}$$

(here, we took (9) into account). Since relation (26) from [1] is valid in the case of a high degree of monolayer undersaturation, we can write Eq. (86) as

$$b_{tr} = 2(2\ \bar{a})^{\frac{1}{2}} / 27 \nu_n^{\frac{1}{2}} \quad (\xi \ll 1) \tag{87}$$

this being Kohler's formula [4] (see [3], Eq. (11)).

Let us discuss the results of calculation of the threshold value b_{tr} of the chemical potential of the vapor in the general theory, with allowance for the dependence of adsorption on the concentration of the solution inside the drop.

Curve I in Fig. 6 shows the dependence of b_{tr} on ν_n described by Eqs. (81-82) with $w = 10$, $x_\alpha = 10^{-5}$, $s_\infty = 1$ (when inequality (32) is not satisfied). A logarithmic scale was used for ν_n. For comparison, curve II shows the dependence of b_{tr} on ν_n according to asymptotic formula (87). This formula is actually valid only if ν_n is sufficiently large ([1], condition (27)). In this case, curve II nearly merges with I. The deviation of I from curve II illustrates the effect of adsorption on the
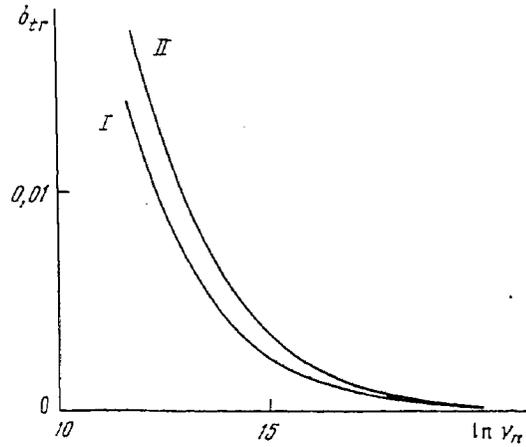
Fig. 6. Dependence of b_{tr} on $\ln \nu_n$ with $w = 10$, $x_\alpha = 10^{-5}$, and $s_\infty = 1$.

threshold value of the chemical potential of the vapor. Let us explore this effect further. We begin with the region of very high values of ν_n (values at which condition (27) from [1] is observed for certain). Adsorption is seen to have little effect on the threshold chemical potential of the vapor in this case (it is not even perceptible in Fig. 6). While small, this effect nonetheless leads (in accordance with Eq. (29) from [1]) to the previously discovered [1] increase in the threshold chemical potential of the vapor when the substance of the condensation nucleus is surface-active (when $s > 0$).

However, the effect of adsorption on threshold chemical potential changes in terms of both sign and magnitude with a decrease in ν_n. Figure 6 convincingly shows that, with a decrease in ν_n, adsorption conversely decreases (and very substantially) the threshold chemical potential of the vapor. The decrease in the latter with a decrease in ν_n occurs within the region of large values of ν_n— where the condition regarding the macroscopic nature of the condensation nucleus $\nu_n >> 1$ is satisfied (this condition corresponds to condition (37) in [3]).

Curves 1-3 in Fig. 7 show the dependence of the extreme values $(b_\nu)_{0i}$ ($i = 1, 2, 3$) of the chemical potential of the condensate b_ν on $\ln \nu_n$ according to Eq. (84) when $w = 20$, $x_\alpha = 10^{-5}$, and $s_\infty = 1$ (when inequality (32) is satisfied). As before, a logarithmic scale is used for ν_n. The extreme values $(b_\nu)_{01}$ and $(b_\nu)_{03}$ are maxima of chemical potential b_ν, while the extreme value $(b_\nu)_{02}$ is a minimum of chemical potential b_ν. This minimum exists only when $\nu_{n_*}^{(a)} < \nu_n < \nu_{n_*}^{(b)}$. In this case, it exists with both maxima. In the region $u < \nu_n < \nu_{n_*}^{(a)}$ there is only one maximum $(b_\nu)_{03}$, while in the region $\nu_n > \nu_{n_*}^{(b)}$ there is only one maximum $(b_\nu)_{01}$. In accordance with (85), the threshold value b_{tr} of the chemical potential of the vapor for each value of ν_n is determined by the highest parts of curves 1 and 3. The maxima $(b_\nu)_{01}$ and $(b_\nu)_{03}$ responsible for the threshold value b_{tr} of the chemical potential of the vapor change places at the point of intersection of curves 1 and 3. Curves 1 and 3 terminate respectively at $(b_\nu)_{01}$ and $(b_\nu)_{03}$. As might be expected, the minimum $(b_\nu)_{02}$ lies below the maxima $(b_\nu)_{01}$ and $(b_\nu)_{03}$.

We make the following observation. With the use of the logarithmic scale for ν_n and ν_0 in Figs. 2-7, it is implied that $\nu_n \geq 1$ and $\nu_0 \geq 1$. Thus, $\ln \nu_n \geq 0$ and $\ln \nu_0 \geq 0$. In this case, the agreement between Figs. 2-7 and formal relations (27-28) is only qualitative.

Direct Calculations of the Chemical Potential of the Condensate with Variable Adsorption. We will illustrate the above analytical findings regarding the extrema of the chemical potential of the condensate b_ν by direct calculation of b_ν as a function of the variable ν with assigned parameters ν_n, x_α, s_∞, and w.

We will proceed on the basis of the general thermodynamic expression presented in [1] for b_ν:

$$b_\nu = -x + (2/3)a\nu^{-1/3} \tag{88}$$

([1], Eq. (9)). We will also take into account Eq. (22) for the material balance in the drop. In light of (7-9), the dependence of the surface tension of the drop a and the amount of adsorption s on concentration x is given by Eqs. (3) and (11).

We use (22) and (11) to obtain a quadratic equation for concentration x (with assigned ν_n, s_α, x_∞). Solving the equation we find
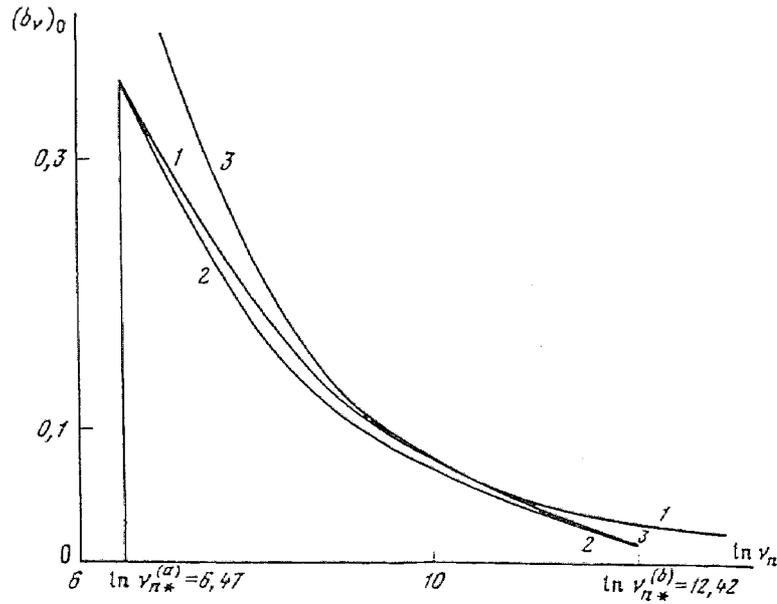
Fig. 7. Dependence of $(b_\nu)_{0i}$ (i = 1, 2, 3) on $\ln \nu_n$ with w
$= 20$, $x_\alpha = 10^{-5}$, $s_\infty = 1$.

$$x = \frac{1}{2}\left(\nu_n \nu^{-1} - s_\infty \nu^{-\frac{1}{3}} - x_\alpha\right) + \frac{1}{2}\sqrt{\left(\nu_n \nu^{-1} - s_\infty \nu^{-\frac{1}{3}} - x_\alpha\right)^2 + 4x_\alpha \nu_n \nu^{-1}} \tag{89}$$

The second root of this equation is negative and is thus of no physical interest.

In accordance with (89), we will have

$$x = \nu_n \nu^{-1} - s_\infty \nu^{-\frac{1}{3}} \to \infty \quad (\nu \to 0) \tag{90}$$

$$x = \nu_n \nu^{-1} \to 0 \quad (\nu \to \infty) \tag{91}$$

Although Eq. (90) and the consequent (by virtue of (3)) approach of a to $-\infty$ as $\nu \to 0$ are of purely formal significance, they nevertheless lead (in accordance with (88)) to the correct result: $b_\nu \to -\infty$ as $\nu \to 0$. This result is not influenced by the fact that the first term in the right side of (88) must be replaced by $-\ln x$ when $x \to \infty$ [3].

The variable ν has no upper bound when allowance is made for the dependence of adsorption on the drop surface on the concentration of the solution inside the drop. This contrasts with the drop model in which adsorption is constant [2]. Relations (88), (3), and (91) are consistent with the general hypothesis that the chemical potential of the condensate b_ν approaches zero from the side of positive values when $\nu \to \infty$.

Figure 8 shows results calculated from formulas (88), (3), (7-9), and (89) to determine chemical potential b_ν as a function of ν. We put $\nu_n = 1000$, $x_\alpha = 10^{-5}$, $s_\infty = 1$, $\bar{a} = 20$, and, accordingly, $w = 20$. As is clear from (68), the inequality $w > w_b$ is satisfied for the chosen parameter values. We also find that $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$ ($\nu_{n*}^{(a)} = 645$, $\nu_{n*}^{(b)} = 2.5 \cdot 10^5$ when $x_\alpha = 10^{-5}$, $s_\infty = 1$, and $w = 20$). Thus, both of the above conditions regarding the simultaneous existence of three extrema of chemical potential b_ν are satisfied. These extrema can be seen in Fig. 8. Their relative location on the axis of the variable ν is consistent with (58).

A decrease in ν_n would cause the left maximum to approach the minimum of chemical potential b_ν. These extrema would even merge at $\nu_n = \nu_{n*}^{(a)}$, leaving chemical potential b_ν with just one (the right) maximum. Conversely, an increase in ν_n would cause the right maximum to approach the minimum of chemical potential b_ν. These extrema would merge at $\nu_n = \nu_{n*}^{(b)}$ and chemical potential b_ν would have only one (the left) maximum.

If, with assigned ν_n and x_α, we were to change s_∞ and $\bar{a}$ so as to decrease the parameter w, the left maximum of chemical potential b_ν would also decrease. At $w = w_b$, the left maximum and minimum of chemical potential b_ν would merge (and only the right maximum would remain at $w < w_b$).

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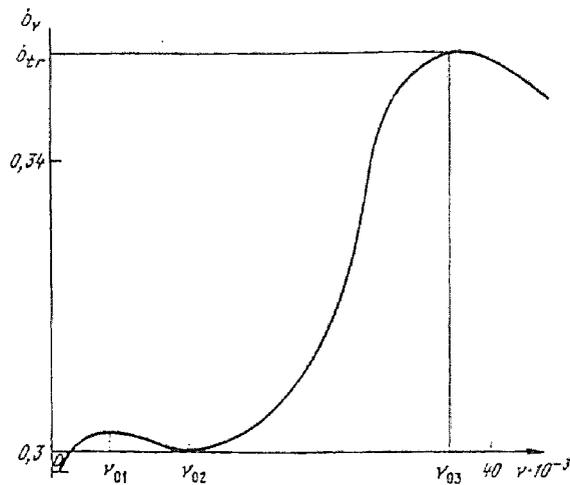
Fig. 8. Chemical potential b_ν as a function of ν with $\nu_n = 1000$, $x_\alpha = 10^{-5}$, $s_\infty = 1$, $w = 20$, and adsorption dependent on concentration.

If we were to instead change s_∞ and $\bar{a}$ so as to increase w for assigned ν_n and x_α, we would see the following pattern. The left maximum of chemical potential b_ν would increase. The minimum of chemical potential b_ν would be moved farther from this maximum and become more distinct. The value of $\nu_{n*}^{(a)}$ would decrease and become nearly equal to ν_{n*} in the drop model with constant adsorption [2]. The value of $\nu_{n*}^{(b)}$, conversely, would increase. As a result, the condition $\nu_{n*}^{(a)} < \nu_n < \nu_{n*}^{(b)}$ for the simultaneous existence of three extrema of chemical potential b_ν would be satisfied (assuming that ν_n is assigned) with a large margin of error.

The extrema of the chemical potential of the condensate b_ν must be studied analytically in order to predict the complex effect of all four external parameters ν_n, x_α, s_∞, and w on b_ν as a function of the variable ν by direct numerical calculation. We should also recall the statement in [2] to the effect that numerical determination of the dependence of chemical potential b_ν on ν yields a result that is valid only for one value of the external parameter ν_n, while analytic relations established between the thermodynamic characteristics of a drop in which the condensate has an extremum of chemical potential embrace the entire range of possible values of the parameter ν_n.

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