

# Calculation and Analysis of Thermodynamic Characteristics for the Condensation Kinetics on the Soluble Nuclei of a Surfactant

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**Abstract** – Experimentally measurable thermodynamic parameters that are necessary for the description of the kinetics of condensation of a supersaturated vapor on the soluble nuclei of a surfactant have been calculated on the basis of strict thermodynamic relationships. The results of the calculation are presented in a form that allows the dependence of the thermodynamic parameters on the adsorption of the matter comprising the nucleus on the surface of a nucleating droplet to be studied as a function of the external parameters involved in the condensation problem. Calculations are performed for the Frumkin adsorption isotherm, which allows for lateral interactions in the adsorbed monolayers of soluble surfactants. The extremal situation, in which the matter comprising the nucleus is almost completely adsorbed on the droplet surface, is considered, and the role of the lateral interaction parameter in the formation of the activation energy for condensation (an important thermodynamic characteristic of the kinetics of condensation) is established. The results of the calculations are shown to have important practical implications. In contrast to popular opinion, the adsorption may both hinder and facilitate the heterogeneous condensation of vapor on the soluble nuclei of a surfactant.

In the previous work [1], we formulated an algorithm for the calculation of experimentally measurable thermodynamic characteristics for the kinetics of a vapor condensation on the soluble nuclei of a surfactant. The algorithm is based on strict thermodynamic relationships and is not restricted to any particular form of adsorption isotherm of the matter comprising the nucleus on the surface of a droplet nucleating on the soluble surfactant.

The use of the algorithm in determining the thermodynamic characteristics in an explicit form requires the knowledge of particular adsorption isotherms. One of these is the Frumkin adsorption isotherm, which is representative from the standpoint of the theory of adsorption monolayers of soluble surfactants [2]. This isotherm allows for lateral interactions in the monolayers.

The purpose of this article was to calculate and analyze the thermodynamic characteristics for the kinetics of vapor condensation on the soluble nuclei of a surfactant by using the algorithm formulated in [1] and the Frumkin adsorption isotherm.

## INITIAL THERMODYNAMIC RELATIONSHIPS

First, we recall the notation used in [1]:  $\nu$  is the number of molecules condensed in a droplet from the vapor phase;  $\nu_n$  is the number of molecules or ions in

the condensation nucleus;  $b_v$  and  $b$  are the chemical potentials of the condensate and vapor, respectively (expressed in thermal energy units  $kT$ , where  $k$  is the Boltzmann constant and  $T$  is the absolute temperature of both vapor and drop), measured from the level corresponding to the equilibrium between vapor and condensed liquid with a flat interface;  $b_{thr}$  is the threshold value of the chemical potential of vapor, above which the vapor condenses on the nucleus without surmounting the activation barrier;  $\Delta F$  is the activation energy for condensation (expressed in thermal energy units  $kT$ );  $x$  is the relative surfactant concentration (i.e., the surfactant: solvent molar ratio) in the bulk solution phase of the droplet;  $a \equiv (36\pi v_1^2)^{1/3} \sigma / kT$  is the dimensionless surface tension of the solution,  $\sigma$  is the surface tension of the solution,  $v_1$  is the molar volume of condensate;  $s \equiv (36\pi v_1^2)^{1/3} \Gamma_n$  is the dimensionless adsorption, and  $\Gamma_n$  is the relative adsorption of the matter comprising the nucleus adsorbed on the droplet surface (the quantity  $sv^{2/3}$  is the total number of molecules or ions of the nucleus adsorbed on the droplet surface).

As established in [1, 3, 4], the domain of interest is in the subthreshold region of vapor metastability,

$$3 \leq \Delta F \leq 30 \quad (1)$$

in which (see double inequality (9) in [1]) the activation barrier for condensation is significant, but can still be surmounted. For the practically important macroscopic sizes of the condensation nuclei (as in [1, 3, 4], only these nuclei are implied in what follows), the subthreshold region of vapor metastability is extremely narrow and occurs only slightly below the threshold value  $b_{thr}$  of the chemical potential of the vapor. The subthreshold region of vapor metastability can be described by the expression

$$b = b_{thr}(1 - \epsilon) \tag{2}$$

(coinciding with relation (2) in [1]), where  $\epsilon > 0$  and  $\epsilon \ll 1$ . The subthreshold region is the most important domain for the kinetic theory of heterogeneous condensation [3, 4].

The threshold value of the chemical potential of the vapor, which is the principal quantity in the theory, is determined by the condition

$$b_{thr} = \max(b_v) \tag{3}$$

(see equation (1) in [1]). Here, the subscript 0 refers to the possible extrema of the chemical potential of condensate, and the symbol max indicates the greatest extremum (naturally, one of the maxima). The quantities corresponding to the greatest extremum will be indicated (as in [1]) by the subscript thr.

The condition of applicability of the thermodynamic theory developed in [1] for the subthreshold region of vapor metastability is given by inequalities

$$\frac{1}{3} (2\epsilon b_{thr})^{1/2} \left| \frac{\partial^3 b_v}{\partial v^3} \right|_{thr} / \left| \frac{\partial^2 b_v}{\partial v^2} \right|_{thr}^{3/2} \ll 1, \tag{4}$$

$$\epsilon < [b_{thr} - (b_v)_0] / b_{thr} \quad ((b_v)_0 < b_{thr}) \tag{5}$$

(see inequalities (10) and (11) in [1]). The former condition ensures the parabolic approximation used in [1] for the dependence of the chemical potential of condensate  $b_v$  on the number of molecules  $v$ . The condition is valid in the vicinity of the point  $v = v_{thr}$  (corresponding to the greatest extremum of the chemical potential of condensate) responsible for the formation of the activation energy  $\Delta F$ . The condition (5) provides for the assumption [1] that the subthreshold region of vapor metastability lies above all extrema of the chemical potential of condensate, except for the greatest one ( $b_{thr}$ ).

### ALGORITHM OF CALCULATION OF THE THERMODYNAMIC CHARACTERISTICS OF CONDENSATION KINETICS

The key quantities for the description of condensation kinetics are the thermodynamic characteristics  $b_{thr}$ ,  $v_{thr}$ ,  $(\partial^2 b_v / \partial v^2)_{thr}$ , and  $\Delta F$ . These thermodynamic parameters of the condensation kinetics are the only ones dealt with below. As has been shown in [1], once these

values are known, all the other experimentally measurable quantities of interest in the general kinetic theory of heterogeneous condensation [4] are readily obtained, including the positions and halfwidths of the potential minimum and potential maximum of the work of droplet formation on the nucleus, expressed as functions of the number of condensate molecules.

An algorithm for the calculation of the thermodynamic characteristics  $b_{thr}$ ,  $v_{thr}$ ,  $(\partial^2 b_v / \partial v^2)_{thr}$ , and  $\Delta F$  of the condensation kinetics as functions of the external parameters of the condensation problem [assuming an arbitrary form of the adsorption isotherm  $x(s)$ ] is formulated in [1]. The selection of the adsorption  $s$  (rather than the concentration  $x$ ) as a variable for the description of the state of a droplet is explained by the fact that  $x(s)$ , unlike the inverse function  $s(x)$ , is always uniquely determined.

The calculation algorithm is essentially as follows. First, the Gibbs adsorption equation

$$\partial a / \partial s = -\partial \ln x / \partial \ln s \tag{6}$$

(equation (14) in [1]) is integrated with the given function  $x(s)$  (adsorption isotherm) to determine the function  $a(s)$  (the equation of state of the surfactant adlayer). If the equation of state  $a(s)$  is initially specified instead of  $x(s)$ , then the integration of (6) is used to determine the function  $x(s)$ .

The function  $a(s)$  is substituted into the expression

$$[2(a/s)z(1-z) - (3-z)^2] \partial a / \partial s = 2(a/s)z^2 \tag{7}$$

(equation (21) in [1]), which determines the extrema of the chemical potential of condensate. Upon solving this equation, considered as a square equation with respect to  $z$ , we obtain (generally speaking, not uniquely) the function  $z(s)$ . According to the definition

$$z \equiv s v_0^{2/3} / v_n \quad (0 \leq z \leq 1) \tag{8}$$

(equation (20) in [1]), the quantity  $z$  represents the fraction of the matter comprising the nucleus adsorbed on the droplet at the extremum of the chemical potential of condensate. For simplicity, we omit the subscript 0 indicating that the adsorption  $s$ , the surface tension  $a$ , and its derivatives with respect to  $s$  (as well as the concentration  $x$  introduced below) correspond to the extrema of the chemical potential of condensate.

Then, the functions  $x(s)$  and  $z(s)$  are substituted into the equation

$$v_n^{1/2} = (s^{3/2} / x) (1-z) / z^{3/2} \tag{9}$$

(equation (23) in [1]), which describes the balance of the matter comprising the nucleus which is dissolved in the droplet. As a result, we arrive to an equation relating  $v_n$  to  $s$ , which is solved with respect to  $s$  to determine (generally speaking, not uniquely) the function  $s(v_n)$ .

Finally, the functions  $a(s)$ ,  $z(s)$ , and  $s(v_n)$  are substituted into the thermodynamic relationship

$$(b_v)_0 = \left(\frac{s}{z}\right)^{3/2} v_n^{-1/2} \left(\frac{2az}{3s} + z - 1\right) \quad (10)$$

(equation (22) in [1]), and also into equation (8) and the relations

$$\begin{aligned} \left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 &= \left(\frac{s}{z}\right)^{9/2} \frac{v_n^{-7/2}}{27(3-z)^3} \left\{ 8\left(\frac{a}{s}\right)^3 z^2(1-z) \right. \\ &\quad - 4\left(\frac{a}{s}\right)^2 z(1-z)(3-z)(6+z) \\ &\quad \left. - 6\frac{a}{s}(3-z)^2(z^2+4z-3) \right. \end{aligned} \quad (11)$$

$$\left. - \left[ 2\frac{a}{s}z(1-z) - (3-z)^2 \right]^3 \frac{s}{z^2} \frac{\partial^2 a}{\partial s^2} \right\},$$

$$\Delta F = \frac{4}{3} \varepsilon^{3/2} b_{\text{thr}}^{3/2} \left[ 2 / \left| \partial^2 b_v / \partial v^2 \right|_{\text{thr}} \right]^{1/2} \quad (12)$$

(equations (26) and (8), respectively, in [1]). Each time, the maximum  $(b_v)_0$  is separated, which, according to equation (3), gives the threshold value  $b_{\text{thr}}$  of the chemical potential of vapor (subscripts 0 and thr are considered as identical). Thus, all the thermodynamic characteristics of the condensation kinetics mentioned above are determined as functions of the external parameters involved in the condensation problem.

## ADSORPTION RENORMALIZATION FACTORS

The effect of adsorption of the soluble matter comprising the nucleus upon the thermodynamic characteristics of the condensation kinetics are conveniently expressed through the quantities

$$f \equiv (b_v)_0 / (\bar{b}_v)_0, \quad (13)$$

$$g \equiv v_0 / \bar{v}_0, \quad (14)$$

$$p \equiv \left(\frac{\partial^2 b_v}{\partial v^2}\right)_0 / \left(\frac{\partial^2 \bar{b}_v}{\partial v^2}\right)_0, \quad (15)$$

$$q \equiv \Delta F / \Delta \bar{F}, \quad (16)$$

where the upper bar indicates the values determined in the absence of the adsorption of the matter comprising the nucleus.

If no surfactant adsorption takes place, the chemical potential of the condensate exhibits a single extremum, specifically, the maximum [3]. The quantities  $(\bar{b}_v)_0$ ,  $\bar{v}_0$ ,  $(\partial^2 \bar{b}_v / \partial v^2)_0$ , and  $\Delta \bar{F}$  are uniquely determined and the

subscript 0 (in the first three) can be assumed to be identical to thr. The principal terms of asymptotics derived in [1] for the case of strong adsorption undersaturation of the matter comprising the nucleus on the droplet surface (equations (37) - (40) in [1]) give for the above parameters:

$$(\bar{b}_v)_0 = 2(2\bar{a}/9)^{3/2} v_n^{-1/2}, \quad (17)$$

$$\bar{v}_0 = (9/2\bar{a})^{3/2} v_n^{3/2}, \quad (18)$$

$$(\partial^2 \bar{b}_v / \partial v^2)_0 = -(2/3)(2\bar{a}/9)^{9/2} v_n^{-7/2}, \quad (19)$$

$$\Delta \bar{F} = (16/6^{1/2}) \varepsilon^{3/2} v_n, \quad (20)$$

where  $\bar{a}$  is the dimensionless surface tension of pure condensate. Equations (17) - (20) have been also obtained in [3].

As was noted above, it is possible that the chemical potential of condensate exhibits several extrema for adsorption of the matter comprising the nucleus on the droplet surface. As a result, the quantities  $(b_v)_0$ ,  $v_0$ ,  $(\partial^2 b_v / \partial v^2)_0$  in (13) - (15) are not uniquely defined and, hence [see (12)], the activation energy  $\Delta F$  in (16) is incompletely determined. The calculation algorithm formulated above allows the entire complicated pattern of extrema in the chemical potential of condensate to be described using the variables  $f$ ,  $g$ ,  $p$ , and  $q$  introduced by equations (13) - (16). The greatest extremum is the only for which  $(b_v)_0 = b_{\text{thr}}$ ; then the corresponding values of the other parameters, the subscript 0, can be replaced by thr.

Assuming the external parameters  $v_n$ ,  $\bar{a}$ , and  $\varepsilon$  to be same with and without the surfactant adsorption on the droplet, it is seen that the quantities  $f$ ,  $g$ ,  $p$ , and  $q$  introduced by equations (13) - (16) are essentially "adsorption renormalization factors." In these terms, all the complicated patterns of adsorption influencing the thermodynamic characteristics of the condensation kinetics can be studied, depending on the external parameters involved in the problem of vapor condensation on the soluble nuclei of the surfactant.

The dependence of the activation energy on the external parameter  $\varepsilon$ , as expressed by equations (12) and (20), exhibits a universal character (proportional to  $\varepsilon^{3/2}$ ). Accordingly, the renormalization factor  $q$  given by (16) does not depend on  $\varepsilon$  (the factors  $f$ ,  $g$ , and  $p$  are primordially independent of  $\varepsilon$ ). Note, however, that the chemical potential of vapor, as determined by equation (2), may differ in the presence and absence of the adsorption, because  $b_{\text{thr}} \neq \bar{b}_{\text{thr}}$ .

In order to find the explicit form of the renormalization factors  $f$ ,  $g$ ,  $p$ , and  $q$  using the above algorithm, we must specify the adsorption isotherm (or the equation of the state of the surfactant adlayer). The Frumkin adsorption isotherm [2] is a representative function used for the description of monolayers of soluble surfactants with an allowance for lateral interactions in the

adlayer. Using the notation adopted in this work, this adsorption isotherm can be written as

$$x = [x_\alpha s / (s_\infty - s)] \exp(-2\kappa s / s_\infty), \quad (21)$$

where  $s_\infty$  is the adsorption capacity of the monolayer of the surfactant,  $x_\alpha$  is the characteristic surfactant concentration such that the ratio  $x_\alpha / s_\infty$  represents the Henry constant, and  $\kappa$  is the parameter of lateral interactions in the monolayer. The corresponding equation of the state of the adsorbed layer of surfactant is obtained by integrating the Gibbs adsorption equation (6):

$$a = \bar{a} + s_\infty [\ln(1 - s/s_\infty) + \kappa(s/s_\infty)^2] \quad (22)$$

(this coincides with equation (54) in [1]). The Frumkin adsorption isotherm provides more information as compared to the Langmuir isotherm used in [5]. At  $\kappa = 0$ , the Frumkin adsorption isotherm transforms into the Langmuir adsorption isotherm, and the equation of state (22), into the van Laar equation.

Expressions (17) - (22) will be used straightforward for the determination of the renormalization factors  $f$ ,  $g$ ,  $p$ , and  $q$  according to the algorithm proposed for the calculation of thermodynamic characteristics of the condensation kinetics. The external parameters for the problem of condensation of saturated vapor on the soluble nuclei of a surfactant reduce to five parameters:  $v_n$ ,  $\bar{a}$ ,  $s_\infty$ ,  $x_\alpha$ , and  $\kappa$ .

### RESULTS OF THE CALCULATION OF THERMODYNAMIC CHARACTERISTICS OF CONDENSATION KINETICS

The results of the calculation of thermodynamic characteristics of condensation kinetics will be presented by plots of the renormalization factors  $f$ ,  $g$ ,  $p$ , and  $q$  versus the external parameter  $\log v_n$  for the given values of the other external parameters ( $\bar{a}$ ,  $s_\infty$ ,  $x_\alpha$ , and  $\kappa$ ). This form of presentation is most informative and illustrative. At the same time, these plots would allow us to analyze the effect of the adsorption of surfactant upon the thermodynamic characteristics of condensation kinetics.

Figures 1 - 3 show the renormalization factors  $f$ ,  $g$ , and  $p$  plotted against  $\log v_n$ . The calculations were performed for a quite realistic set of values:  $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ . The parameter  $\kappa = 1.95$  was selected for the following reasons. This value, on the one hand, is below the level  $\kappa = 2$  (where the Frumkin isotherm exhibits a phase transition in the monolayer) and, on the other hand, is sufficiently large to reveal the role of lateral interactions. The set of values adopted for the parameters  $\bar{a}$ ,  $s_\infty$ ,  $x_\alpha$ , and  $\kappa$  is also of interest because it refers to the most complicated situation, whereby the renormalization factors  $f$ ,  $g$ , and  $p$  have intervals of non-unique determination on the  $\log v_n$  axis. In these intervals (specifically,  $8.7 \leq \log v_n \leq 9.0$  and  $13.5 \leq \log v_n \leq 14.3$ ), the chemical potential of

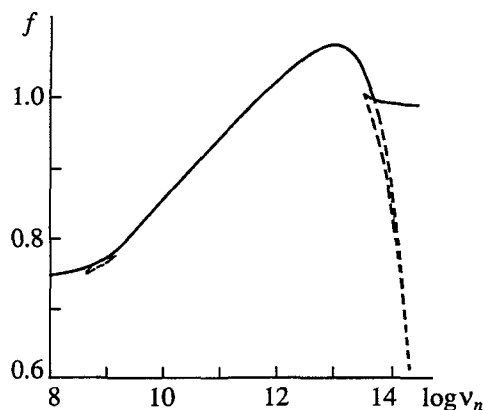


Fig. 1. Renormalization factor  $f$  versus  $\log v_n$  for the Frumkin adsorption isotherm;  $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ .

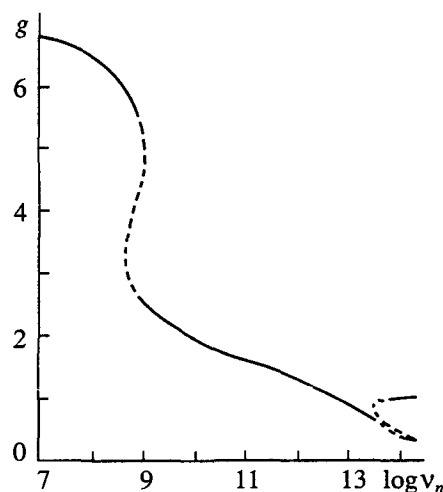


Fig. 2. Renormalization factor  $g$  versus  $\log v_n$  for the Frumkin adsorption isotherm;  $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ .

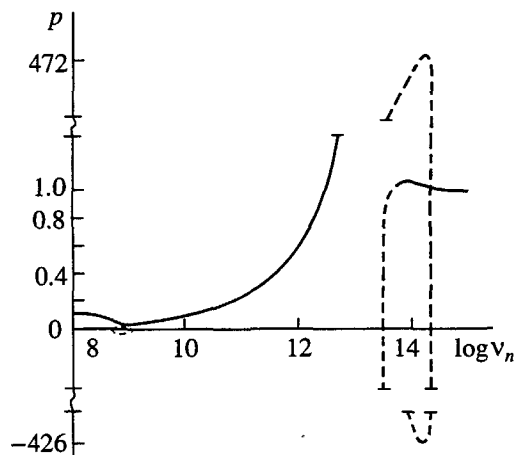


Fig. 3. Renormalization factor  $p$  versus  $\log v_n$  for the Frumkin adsorption isotherm;  $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ .

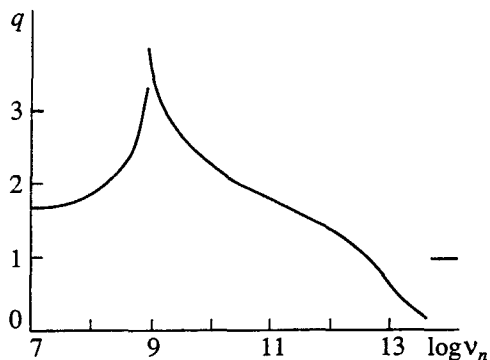


Fig. 4. Renormalization factor  $q$  versus  $\log v_n$  for the Frumkin adsorption isotherm;  $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ .

condensate exhibits three extrema – two maxima separated by a minimum. Inside the intervals, there are points on the  $\log v_n$  axis corresponding to a change of the absolute maximum of the chemical potential of condensate (i.e., those determining the threshold value  $b_{thr}$  of the chemical potential of vapor). In Figs. 1 - 3, the solid curves show the behavior of the renormalization factors  $f$ ,  $g$ , and  $p$  corresponding to the absolute maxima of the chemical potential of condensate, which is the only information of interest from the standpoint of physics. The quantity  $f$  determines the ratio  $b_{thr}/\bar{b}_{thr}$  and is naturally represented by a continuous line. The plots for  $g$  and  $p$  exhibit breaks (apparently not pronounced in Fig. 3) at the points corresponding to the change of the absolute maximum of the chemical potential of condensate. For the sake of completeness, the dashed lines in Figs. 1 - 3 show the variation of the renormalization factors  $f$ ,  $g$ , and  $p$  corresponding to the lower maximum (of the two simultaneously existing ones) and the minimum in the chemical potential of condensate (the determination of this behavior is provided by the calculation algorithm).

Figure 4 shows the dependence of the renormalization factor  $g$  on  $\log v_n$  for the same external parameters as above ( $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ ), plotted with the curves of Figs. 1 - 3 taken into account. The breaks in the plots of  $q$  versus  $\log v_n$  occur at the same points of change in the absolute maximum of the chemical potential of condensate. In the vicinity of these points on the  $\log v_n$  axis, condition (5) is invalid and equation (12) for the activation energy  $\Delta F$  is inapplicable. Neither can we use at these points the plot for the quantity  $q$  [introduced by equation (16)] depicted in Fig. 4.

In particular, there is a point  $\log v_n \approx 8.9$  on the  $\log v_n$  axis at which the absolute maximum of the chemical potential of condensate exhibits a change. For the above values of the parameters  $\bar{a}$ ,  $s_\infty$ ,  $x_\alpha$ , and  $\kappa$ , the double inequality (1) reduces in the vicinity of this

point to the condition  $2 \times 10^{-7} \leq \varepsilon \leq 10^{-6}$ . The requirement of compatibility of the upper limit  $10^{-6}$  for the variation of  $\varepsilon$  with the condition (5) implies that  $[b_{thr} - (b_v)_0]/b_{thr} \geq 10^{-6}$  [ $(b_v)_0 < b_{thr}$ ]. This requirement excludes from consideration only an extremely narrow interval in the  $\log v_n$  axis (not shown in Fig. 4) in the vicinity of the point  $\log v_n \approx 8.9$ . In this interval, equation (12) for the activation energy is inapplicable and, accordingly, the plot of Fig. 4 for the renormalization factor  $q$  cannot be used.

The upper limit  $10^{-6}$  for variation of the parameter  $\varepsilon$  in the subthreshold region of vapor metastability is also compatible (with considerable reliability) with inequality (4). For the values of the parameters  $\bar{a}$ ,  $s_\infty$ ,  $x_\alpha$ , and  $\kappa$  adopted above, this inequality reduces near the point  $\log v_n \approx 8.9$  on the  $\log v_n$  axis to the condition  $\varepsilon \leq 2 \times 10^{-3}$ . Here, the third derivative  $(\partial^3 b_v / \partial v^3)_{thr}$  was estimated using the asymptotic expression for  $z \approx 1$  (see equation (49) in [1]).

As was noted in [1], the maxima of the chemical potential of condensate can be reached not only upon the complete dissolution of the nucleus in the droplet (as was assumed in [1] and in this paper), but may also correspond to the formation of a liquid film on the nucleus which is partially dissolved in the droplet [6]. This case is characterized by smaller values of  $\log v_n$  at the break points of the activation energy, and wider intervals at these points on the  $\log v_n$  axis, in which the activation energy cannot be analytically determined.

#### ACTIVATION ENERGY FOR THE CASE OF VIRTUALLY COMPLETE ADSORPTION OF THE MATTER COMPRISING A NUCLEUS ON THE DROPLET SURFACE

Now we will consider a comparatively simple, but practically important limiting situation, whereby the matter comprising a nucleus of condensate is almost completely adsorbed on the droplet surface. In this case, the quantity  $z$ , defined by equation (8) representing the adsorbed fraction of the matter comprising the nucleus, is very close to its upper variation limit (equal to unity), which can be expressed by the inequality

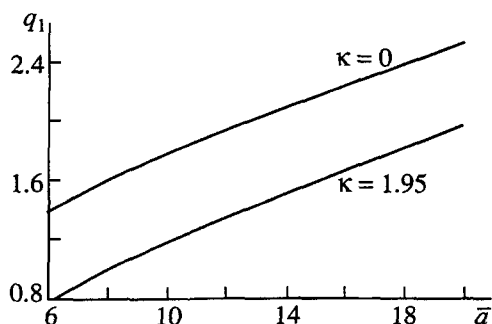
$$1 - z \ll 1 \quad (23)$$

(equation (41) in [1]). As was shown earlier [1], in this case the chemical potential of condensate exhibits a single extremum (naturally, the maximum).

In order to simplify the analysis, we will consider a single thermodynamic characteristic of the condensation kinetics, namely, the activation energy  $\Delta F$ . This parameter is given by the equation

$$\Delta F = \frac{16a_1 \varepsilon^{3/2} v_n}{6^{1/2} 3s_1} \left[ 1 - \frac{4s_1^2}{3a_1} \left( \frac{\partial^2 \bar{a}}{\partial s^2} \right)_1 \right]^{-1/2} \quad (24)$$

(equation (48) in [1]). Here, the index 1 indicates the values corresponding to  $z = 1$ . The method of determi-



**Fig. 5.** Renormalization factor  $q_1$  versus the parameter  $\bar{a}$  for the Frumkin adsorption isotherm;  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 0$  or 1.95.

nation of the  $a_1$ ,  $s_1$ , and  $(\partial^2 a / \partial s^2)_1$  values using the above calculation algorithm (and the Frumkin adsorption isotherm) is described in [1].

For the adsorption renormalization factor  $q$  (representing the activation energy), which is denoted in this case by  $q_1$ , equations (16), (20), and (24) yield:

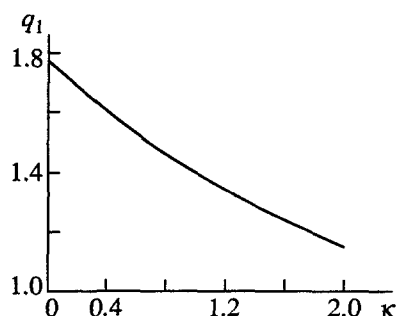
$$q_1 = \frac{a_1}{3s_1} \left[ 1 - \frac{4s_1^2}{3a_1} \left( \frac{\partial^2 a}{\partial s^2} \right)_1 \right]^{-1/2}. \quad (25)$$

According to formula (25), the renormalization factor  $q_1$  depends neither on the parameter  $\varepsilon$ , nor on the parameter  $v_n$ .

Figures 5 and 6 show the patterns of variation of the renormalization factor  $q_1$  calculated using equation (25). It is seen that for the fixed parameter  $\kappa$ , the  $q_1$  value increases almost linearly with  $\bar{a}$ . If the parameter  $\bar{a}$  is fixed, the renormalization factor  $q_1$  decreases with growing parameter  $\kappa$ .

## DISCUSSION OF RESULTS

The renormalization factors depicted in Figs. 1 - 4 tend to the limiting values independent of  $v_n$  in the left and right ends of the  $\log v_n$  axis. As the  $\log v_n$  variable moves on the right, the normalization factors tend to the limiting values that are close to unity. The left and right ends of the  $\log v_n$  axis correspond to two extremal situations, when the adsorption of the matter comprising the nucleus on the droplet surface is either strongly undersaturated or almost complete, respectively. Both extremal situations were considered in [1]. The tendency of the renormalization factors in Figs. 1 - 4 to unity in the right-hand asymptotic part of the  $\log v_n$  axis is an obvious result, which needs no comment. The tendency of the renormalization factors to limiting values (independent of  $v_n$ ) in the left-hand asymptotic part of the  $\log v_n$  axis is explained by the fact (see the end of [1]) that the principal terms of asymptotic expressions obtained for the thermodynamic characteristics of the condensation kinetics exhibit the same character of



**Fig. 6.** Renormalization factor  $q_1$  versus the parameter  $\kappa$  for the Frumkin adsorption isotherm;  $\bar{a} = 10$ ,  $s_\infty = 1$ , and  $x_\alpha = 10^{-5}$ .

dependence on  $v_n$  in both extremal cases of the surfactant adsorption on the droplet surface.

The domain of the  $\log v_n$  variation, in which the thermodynamic theory [1] is applicable and the corresponding calculations are valid, can be readily extended in Figs. 1 - 4 to the left up to  $\log v_n \approx 3$  (see restriction (52) in [1]). In this case, the renormalization factors would become still closer to their limiting values in the left-hand asymptotic part of the  $\log v_n$  axis. Thus, the results of calculations presented in Figs. 1 - 4 are valid within the wide range of  $3 \leq \log v_n \leq 16$ . This interval almost covers (at small  $\log v_n$  values) or even extends over (at large  $\log v_n$  values) the range  $1 \leq \log v_n \leq 13$  established in [1] for the dimensions of nuclei of a surfactant encountered in practice. Only the nuclei whose dimensions cannot be considered macroscopic are excluded from consideration.

In concluding, note again the realistic character of the set of external parameters ( $\bar{a} = 15$ ,  $s_\infty = 1$ ,  $x_\alpha = 10^{-5}$ , and  $\kappa = 1.95$ ) adopted in Figs. 1 - 4 as supplementary to the external parameter  $\log v_n$ . This fact makes the results of calculations of the thermodynamic characteristics of condensation kinetics on soluble nuclei of a surfactant practically significant, and demonstrates the wide possibilities of the calculation algorithm proposed in [1].

Figures 5 and 6 show a practically important pattern of variation of the activation energy calculated as a function of the parameter  $\kappa$ , which accounts for lateral interactions in the monolayer, and the parameter  $\bar{a}$ , which represents the dimensionless surface tension of pure condensate.

It is worth specially noting the nonmonotonic variation of the renormalization factor  $f$  with increasing  $\log v_n$  (Fig. 1). As a result of this, the  $\log v_n$  axis has both the region in which  $f > 1$  (i.e.,  $b_{\text{thr}} > \bar{b}_{\text{thr}}$ ) and the region of  $f < 1$  ( $b_{\text{thr}} < \bar{b}_{\text{thr}}$ ). Therefore, the surfactant adsorption can both increase and decrease the threshold value of the chemical potential of vapor. This implies, in

contrast to popular opinion, that the adsorption may both hinder and facilitate the condensation of heterogeneous vapor on the soluble nuclei of a surfactant.

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