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The mutual effects of deliquescence, micellization and adsorption in the thermodynamics of condensation on surfactant nuclei

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We have found the mutual effect of deliquescence, micellization and adsorption on the value of the vapour chemical potential at the threshold for barrierless condensation on soluble surfactant particles; the results are presented in the form of a curve of the threshold value *versus* initial size of the dry surfactant particles serving as the centres of condensation.

The problem of heterogeneous nucleation is of general interest in view of its fundamental nature and variety of performance. The problem becomes most complicated in the case of nuclei of soluble surfactants where we need to consider not only adsorption and condensation out of vapour onto the nuclei, but also dissolution, adsorption and micellization of the nuclear matter within arising drops. At this the nucleus itself can be dissolved partially or completely. The presence of several maxima in the curve of the chemical potential of condensate *versus* the drop size, corresponding to different stages of solution within the drop, is a typical situation. The most important is the largest of the maxima, because it determines the value of the vapour chemical potential at the threshold of barrierless condensation on soluble particles of a given dry size. The behaviour of the threshold value in the case of complete dissolution of a surfactant nucleus in the drop producing the molecular solution, which is realised for certain large sizes of dry nuclei, was presented earlier.[1–3] The goal of the communication is to present a combined analysis of all fundamental factors having an influence on the threshold value of the vapour chemical potential in the situation where the factors are mutually competitive. This will allow us to establish how the threshold value of the vapour chemical potential depends on the initial size of nuclei. The latter is needed for a prediction of condensation activity for nuclei of a specified size and composition and has not been done before.

Let μ be the extreme value of the condensate chemical potential *versus* the drop size. Using μ and $\bar{\mu}$ for the value of the condensate chemical potential at the equilibrium of the condensate with vapour at their flat interface and for the extreme value in the case of complete dissolution of a nucleus in a drop in the absence of adsorption of the nuclear matter, let us define the renormalised dimensionless extreme chemical potential of the condensate in the form $f = (\mu - \mu\ )/(\bar{\mu} - \mu\ )$. It is reasonable to consider the solution of the surfactant nuclear matter in condensing drop to be diluted. Below we will use the relationship $\bar{\mu} = \mu\ + v_1\sqrt{2\bar{\sigma}^3/9\pi}\sqrt{kT\nu_\mathrm{n}}$ which represents Kohler's formula[4] for the extreme value of the condensate chemical potential in the case of dilute solution of the nuclear matter within a drop. Here $\bar{\sigma}$ stands for the surface tension of the condensate in the absence of adsorption of the nuclear matter, v_1 is the volume per molecule of the condensate in the liquid state, ν_n is the number of molecules (or ions) of the nuclear matter in the solution (the number characterises the size of dry nucleus), k is the Boltzmann constant and T is the temperature of the drop and surrounding vapour–gas medium.

If the solution within a drop is molecular and the dissolution of a surfactant nucleus is complete, the corresponding shifted extreme chemical potential f_m is determined as[1]

$$f_\mathrm{m} = \frac{1}{2}\ \frac{9kT\Gamma}{2\bar{\sigma}z}^{3/2}\ \frac{2\bar{\sigma}z}{3kT\Gamma} + z - 1\ . \qquad (1)$$

Here Γ is the surfactant adsorption at the drop surface, z is the fraction of nuclear matter adsorbed at the drop surface, with respect to its total amount in the drop, and σ is the drop surface tension. All of these quantities are referred to an extreme of the condensate chemical potential. The quantities z and σ are dependent of Γ, and Γ depends on the size of the dry nucleus which we characterize by ν_n. The forms of these dependencies are associated with the choice of the specific adsorption isotherm. Nevertheless, it can be shown that the asymptotic form for f_m in the vicinity of $z = 1$ (or at $\nu_\mathrm{n}^{1/2} << 6\pi^{1/2}\nu_1\Gamma_1^{3/2}/x_1$) can be written for an arbitrary adsorption isotherm as

$$f_\mathrm{m}\ \ \frac{9}{2}\frac{\sigma_1}{\bar{\sigma}}\ \frac{kT\Gamma_1}{2\bar{\sigma}}^{1/2} + \frac{9}{4}\pi^{-1/2}x_1\ \frac{\sigma_1}{3kT\Gamma_1} - 1\ \ \frac{kT}{2\bar{\sigma}\nu_1^{2/3}}^{3/2}\nu_n^{1/2}\ , \qquad (2)$$

The notation x stands for the relative concentration (per one molecule of condensate, *i.e.* the molar ratio) of the nuclear matter in the solution within drop. The subscript 1 identifies quantities at $z = 1$. The concentration x_1, the adsorption Γ_1 and the surface tension σ_1 are linked by the equation of state, by the adsorption isotherm, and by the equation $\sigma/\ \Gamma|_{\Gamma=\Gamma_1} = -\sigma_1/2\Gamma_1$ which follows from the equation for an extreme of the condensate chemical potential at $z = 1$.[1,2]

The validity of equation (1) in the case of nuclei of colloidal surfactant assumes that the solution concentration within the condensing drop does not exceed the critical micelle concentration. If this does happen, an additional maximum, contributed by micellization, appears in the curve of the condensate chemical potential *versus* drop size. In the case of a dilute solution of micelles that is unnecessarily related to the fact that the molecular solution is diluted, the corresponding shifted extreme chemical potential f_M (coexisting with f_m in the same curve) is determined as[5]

$$f_\mathrm{M} = \frac{[\sigma_\mathrm{M}(n_\mathrm{M} + z_\mathrm{M})/\bar{\sigma} + 3kT\Gamma_\mathrm{M}(z_\mathrm{M} + 1)/2\bar{\sigma}]^{3/2}}{(n_\mathrm{M} + z_\mathrm{M})(z_\mathrm{M} + 1)^{1/2}} -$$

$$-\frac{9}{4}\pi^{-1/2}x_\mathrm{cmc}\frac{n_\mathrm{M} - 1}{n_\mathrm{M} + z_\mathrm{M}}\ \frac{kT}{2\bar{\sigma}\nu_1^{3/2}}^{3/2}\nu_\mathrm{n}^{1/2}. \qquad (3)$$

Here n_M and z_M are the aggregation number and the charge number for a micelle in the solution, x_cmc is the molar ratio for the critical micelle concentration, the surface tension σ_M and the adsorption Γ_M are referred to the molar ratio x_cmc. Equation (3) is applicable to nuclei of soluble ionic and non ionic colloidal surfactant [we should set in equation (3) $z_\mathrm{M} = 0$ in the latter case]. The requirement that the solution of micelles in a drop should be diluted imposes limitations from below on the attainable values of ν_n in the theory.[5,6] Since we are interested in understanding the principal behaviour of the threshold value of the vapour chemical potential *versus* nuclear size, we will not consider the limitations here.

Let us now take into consideration the very early stage of heterogeneous drop formation when the condensation nucleus is not completely dissolved in the drop. The most important part of this stage is associated with the formation of a thin liquid solution film around the nucleus which practically retains its initial size (the deliquescence stage[7]). Due to the disjoining pressure of the film, the condensate chemical potential

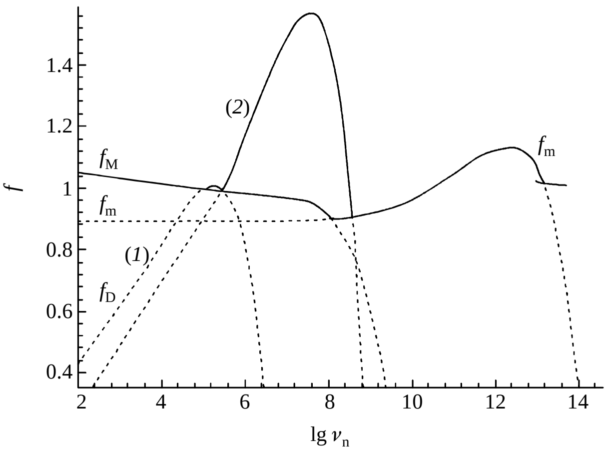

Figure 1 The dependence of the shifted dimensionless extreme chemical potential of condensate, f on lg ν_n. Curve (*1*) corresponds to f_D at $x_D = 0.1$ and $\nu_l/\nu_n = 0.1$. Curve (*2*) corresponds to f_D at $x_D = 0.01$ and $\nu_l/\nu_n = 0.027$.

achieves,[8] within a very thin region of the drop size, its additional maximum. The corresponding shifted extreme chemical potential f_D (coexisting with f_m and f_M in the same curve in the case of nuclei of a colloidal surfactant) can be rewritten[6] in the form

$$f_D = \frac{3^{5/3}\sigma_D}{2\,\bar{\sigma}}(4\pi)^{-1/6}\left(\frac{kT}{2\bar{\sigma}\nu_l^{2/3}}\right)^{1/2}\left(\frac{\nu_l}{\nu_n}\right)^{1/3}\nu_n^{1/6} - \\ -\frac{9}{4}\pi^{-1/2}\left(\frac{z_M+1}{n_M+z_M}x_D + \frac{n_M-1}{n_M+z_M}x_{cmc}\right)\left(\frac{kT}{2\bar{\sigma}\nu_l^{2/3}}\right)^{3/2}\nu_n^{1/2}. \quad (4)$$

Here the molar ratio x_D corresponds to the solubility limit for the surfactant in the solution (the corresponding concentration should be regarded as a gross concentration in the case of solutions of colloidal surfactants), the surface tension σ_D is referred to the molar ratio x_D, ν_n is the volume per molecule (or ion) of the surfactant in the nucleus. Setting $z_M = 0$ or $n_M = 1$ converts equation (4) to the case of nuclei of non-ionic or, correspondingly, of non-colloidal surfactants. In the last case, equation (4) has the widest validity domain in the variable ν_n.

An analytical form, and the similarity of equations (2)–(4), have been reached due to the fact that the concentration of nuclear matter in the solution within a drop does not depend on ν_n in the situations described by these equations. Respectively, the concentration is equal to x_1 at adsorption of almost total amount of the nuclear matter at drop surface, to the critical micelle concentration x_{cmc}, and to the solubility limit x_D.

The completed dependencies of quantities f_m, f_M and f_D on lg ν_n are presented in Figure 1. To compute f_m we used the algorithm desribed earlier[1,2] and the Frumkin equation[1] of state for a surfactant monolayer $\sigma = \bar{\sigma} + kT\Gamma\ [\ln(1-\Gamma/\Gamma\ ) + k(\Gamma/\Gamma\ )^2]$ and the adsorption isotherm $x/x_\alpha = [\Gamma/(\Gamma - \Gamma)] \times \exp(-2k\Gamma/\Gamma\ )$. We set parameters as follows: $T = 300$ K, $\bar{\sigma} = 74\times10^{-3}$ N m^{-1}, $\nu_l = 3\times10^{-29}$ m^3 (water as the condensate), $\Gamma\ = 2\times10^{18}$ molecule m^{-2}, $x\ = 10^{-5}$, $k = 1.95$. We used for the micellar solution of the surfactant, $\sigma_M = \sigma_D = 30\times10^{-3}$ N m^{-1}, $\Gamma_M = \Gamma\ $, $n_M = 119$, $z_M = 9$, $x_{cmc} = 1.5\times10^{-4}$ which seem reasonable in the case of a micellar solution of sodium dodecylsulfate in water. Two values were taken for the solubility limit, $x_D = 0.1$ and $x_D = 0.01$, and for the ratio of molecular volumes of the condensate and of the surfactant in nucleus, $\nu_l/\nu_n = 0.1$ and $\nu_l/\nu_n = 0.027$. As can be seen from equation (4) and from curves (*1*) and (*2*) in Figure 1, the behaviour of f_D is very sensitive to these parameters.

The vapour chemical potential at the threshold for barrierless condensation on soluble nuclei as a function of nuclear size is depicted in Figure 1 by solid lines. Broken lines depict the behaviour of coexisting maxima of the condensate chemical potential which are not significant for a prediction of the threshold point. It is evident that due to the micellization in condensing drops, there is a region in the lg ν_n axis where the threshold value of the vapour chemical potential may be larger than it would be in the case of the surface-inactive nuclei of the same size. The same is true for the deliquescence process in the vicinity of the point

$$(\nu_n)_D = \frac{4\pi}{81\nu_n}\left(\frac{2\sigma_D\nu_l}{kT}\right)^3 \Big/ \left(\frac{z_M+1}{n_M+z_M}x_D + \frac{n_M-1}{n_M+z_M}x_{cmc}\right)^3 \quad (5)$$

which is a point in the maximum of f_D as a function of ν_n. To the left of this point in the lg ν_n axis, f_D can be smaller than f_M and even smaller than f_m (the latter is important for the case of non-colloidal surfactants).

The whole behaviour of the threshold value of the vapour chemical potential is as follows. At large lg ν_n, in the region of the molecular solution of the nuclear matter in a drop, the threshold value increases with decreasing lg ν_n, and the higher the parameter k of the lateral interactions in the monolayer the higher the increase. At smaller lg ν_n, the increase turns on to decrease until the point $f_m = f_M$ or $f_m = f_D$ is reached. If the point $f_m = f_M$ is reached first (which corresponds to curve (*1*) in Figure 1), then we have a growth of the threshold value until the point $f_M = f_D$ and even the point lg$(\nu_n)_D$ are reached. After the point lg $(\nu_n)_D$, we have a decrease in the threshold value until the point $f_D = f_M$ or, for nuclei of non-colloidal surfactants, $f_D = f_m$. To the left of the point $f_D = f_M$ or $f_D = f_m$, the threshold value either grows or, correspondingly, stays fixed. The deliquescence process does not determine the threshold value of the vapour chemical potential in this region of small lg ν_n. Micellization in the case of nuclei of colloidal surfactants, or molecular solution in the case of nuclei of non-colloidal surfactants, becomes important in this region again. If the point $f_m = f_D$ is reached before the point $f_m = f_M$ (which corresponds to curve (*2*) in Figure 1), then we have an increase in the threshold value up to the point lg$(\nu_n)_D$. After the point lg$(\nu_n)_D$ we have the previous picture with the difference that the micellization starts to play a role for the first time. Evidently, the curve depicting f_M should be dropped in the absence of micellization, and the solid line will depict the curve for f_m in the region where f_m will determine the threshold value of the vapour chemical potential.

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References

1 F. M. Kuni, A. K. Shchekin, T. M. Yakovenko and A. I. Rusanov, *Mendeleev Commun.*, 1995, 202.
2 A. K. Shchekin, F. M. Kuni, T. M. Yakovenko and A. I. Rusanov, *Colloid Journal*, 1995, **57**, 93.
3 A. K. Shchekin, F. M. Kuni, T. M. Yakovenko and A. I. Rusanov, *Colloid Journal*, 1995, **57**, 242.
4 F. M. Kuni, A. K. Shchekin and A. I. Rusanov, *Kolloidn. Zh.*, 1993, **55**, 34 [*Russ. Colloid J.* (*Engl. Transl.*), 1993, **55**, 174].
5 A. K. Shchekin, A. I. Rusanov and F. M. Kuni, *Kolloidn. Zh.*, 1993, **55**, 91 [*Russ. Colloid J.* (*Engl. Transl.*), 1993, **55**, 227].
6 F. M. Kuni, A. K. Shchekin and A. I. Rusanov, *Kolloidn. Zh.*, 1993, **55**, 80 [*Russ. Colloid J.* (*Engl. Transl.*), 1993, **55**, 686].
7 J.-P. Chen, *J. Atmos. Sci.*, 1994, **51**, 3505.
8 A. K. Shchekin, A. I. Rusanov and F. M. Kuni, *Kolloidn. Zh.*, 1993, **55**, 185 [*Russ. Colloid J.* (*Engl. Transl.*), 1993, **55**, 776].

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