Russian Chemical Bulletin, International Edition, Vol. 60, No. 6, pp. 1203—1208, June, 2011

Can reverse micelle shells limit nanoparticle growth?

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The possibility to limit the growth of nanoparticles synthesized in reverse microemulsions by the shells of reverse micelles is analyzed theoretically. At surface tension higher than about 30 mJ m^{-2}, the reverse micelle shells cannot inhibit the particle growth. At lower surface tension values, the particle growth can be limited, but the synthesized particles should be much larger than the initial micelles.

Key words: reverse micelles, nanoparticles.

Reverse micelles represent water nanodrops covered with a surfactant monolayer. A reverse microemulsion is a thermodynamically stable solution of reverse micelles in a nonpolar organic solvent. Reverse micelles are often considered as nanoreactors for various chemical reactions. Therefore, the water core of a reverse micelle is called "pool" while the surfactant monolayer on the surface of the reverse micelle is called "shell". An essential feature of chemical reactions in reverse microemulsions is that the reverse micelles can, with some probability, exchange the content of their water pools through collisions with one another. This allows one to consider the totality of water pools as a continuous aqueous pseudophase. Most often, spherical reverse micelles are regarded as nanoreactors. The size of such micelles is mainly determined by the ratio of the molar concentrations of water and surfactant, which is usually denoted as W = [water]/[surfactant]. Simple geometric considerations[1,2] lead to a linear dependence of the micelle pool size on W:

$$R = \frac{3\nu_{\mathrm{H_2O}}}{a_0}W + \frac{3\nu_{\mathrm{H}}}{a_0}, \qquad (1)$$

where R is the water pool radius; $\nu_{\mathrm{H_2O}}$ = 30 Å is the average volume of water molecules in the liquid phase, v_{H} is the volume of the polar part of the surfactant molecule, and a_0 is the surface area per surfactant molecule at the water—oil interface. Owing to the existence of relation, in qualitative treatment the size of reverse micelles and their molar ratio W are often used as synonyms.

Sodium bis-2-ethylhexylsulfosuccinate (Aerosol OT, AOT) is one of the best-studied surfactants used for the preparation of reverse microemulsions. AOT-based reverse microemulsions have a spherical shape and can solubilize a rather large amount of water,[3] namely, up to $W \approx 125$ in n-hexane at 17 °C;[4] however, the maximum possible W ratio is usually about 60. The published data on the sizes and aggregation numbers of AOT reverse micelles are to some extent contradictory. Data averaging by the least squares method gives a_0 = 63 Å^2 and v_{H} = 222 Å^3.[5] Using expression (1), one gets $R \approx (1.4W + 11)$ Å for the water pool radius of AOT reverse micelles.

Since the early 1980s, reverse microemulsions are used for the synthesis of nanoparticles.[6] The most widely used synthetic procedure involves mixing two microemulsions whose aqueous pseudophases contain substances that react to form nanoparticles. The use of reverse microemulsions for the synthesis of nanoparticles was usually based on the assumption that reverse micelle shells inhibit particle growth when the particle size becomes equal to the pool size.[7—10] It was assumed that such a restriction of particle growth allows one to control the size of the synthesized particles by varying the molar ratio W. In addition, based on the assumption that reverse micelles are monodisperse, it was expected that particles synthesized in the micelles should be monodisperse too.[10—14] However, this concept of particle growth restriction by the shells of reverse micelle contradicts experimental data. First, the synthesized particles are usually much larger in size than water pools.[15,16] In some studies, no correlation between the pool size and particle size was reported.[17—19] In this connection, many authors consider control rather than restriction of the particle size by the water pool size. Second, reverse micelles are polydisperse[1,5,20] and thus unsuitable for producing monodisperse particles. Third, the growth of monodisperse particles in reverse micelles occurs rarely; most often, particles show polydispersity of the order of 20—30%. In this study, we theoretically analyze the possibility of nanoparticle growth restriction by reverse micelles. The numerical estimates presented were obtained for AOT-based reverse microemulsions because

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 1177—1182, June, 2011.

this surfactant is most widely used for the synthesis of nanoparticles in reverse microemulsions.

The possibility of nanoparticle growth restriction by micelle shells: an analysis. We assume that particles are spherical and monodisperse. Here, particle growth implies a decrease in the number of particles and a constant total volume of all particles; this corresponds to the Ostwald ripening and coagulation conditions. Thus, particle growth is driven by the decrease in their total surface energy. Until the particle size is smaller than the water pool sizes of reverse micelles, particle growth is unrestricted. Once the particle size becomes equal to the water pool size, further particle growth is restricted by micelle shells. Since the micelle shells are not rigid, the reverse micelles should increase their size due to exchange of water and surfactant molecules with other reverse micelles under the pressure of the growing particles. As a result, the micelle size distribution deviates from the equilibrium one and becomes bimodal, which leads to an increase in the total Gibbs free energy of the micelles. Thus, as the particle grows, its surface energy decreases but the Gibbs free energy of reverse micelles increases. Particles grow until some reach the critical size that corresponds to the minimum value of the total Gibbs free energy of the system.

Now we will show that the change in the Gibbs free energy, ΔG_{full}, of the system comprising the reverse micelles and the growing particles can be calculated as the sum of independently calculated terms:

$$\Delta G_{\mathrm{full}} = \Delta G_{\mathrm{mic}} + \Delta G_{\mathrm{part}}, \qquad (2)$$

where ΔG_{mic} is the change in the Gibbs free energy of the reverse micelles that accompanies the passage to the bimodal size distribution ignoring the growing particles, ΔG_{part} is the change in the Gibbs free energy of the growing particles ignoring the fact that the particles grow within the reverse micelles. Now imagine the particle growth in reverse micelles as a sequence of hypothetical steps (Fig. 1) and include the water reservoir. Step (*1*) involves the reverse micelles whose water pools are filled with particles. On going to step (*2*), particles are transferred to the water reservoir and the volume previously occupied by the particles is now occupied by water from the reservoir. On going to step (*3*) one gets a bimodal micelle size distribution. Step (*4*) corresponds to particle growth. On going to step (*5*) the grown particles are transferred to large micelles and the excess water from the reverse micelles is transferred to the water reservoir. On going from step (*2*) to step (*3*) and from step (*3*) to step (*4*), the Gibbs free energy changes by ΔG_{mic} and ΔG_{part}, respectively. On going from step (*1*) to step (*2*) and from step (*4*) to step (*5*), the Gibbs free energy remains unchanged. The latter statement is substantiated as follows. Except for a thin layer near the micelle shell, water in a reverse micelle has the same properties as conventional water at a negative pressure. The negative pressure is produced because the micelle shell tends to attain the natural curvature and decreases in absolute value as the micelle size increases. The negative pressure affects the Gibbs free energy in accordance with the general equation:

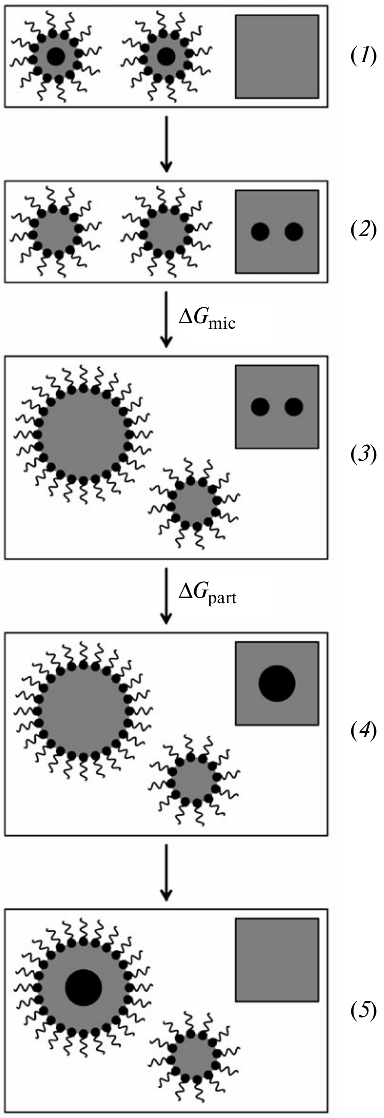

Fig. 1. Thermodynamic chain illustrating the possibility of independent consideration of the changes in the Gibbs free energies of reverse micelles and particles growing in them. Water is shown in grey, grey rectangles denote water reservoirs, grey circles denote the water pools in reverse micelles, and black circles in the water reservoirs and micelles denote particles. Numbers (1)—(5) denote the hypothetical steps of particle growth in reverse micelles.

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P, \qquad (3)$$

where G is the Gibbs free energy, S is the entropy, T is absolute temperature, V is the volume, and P is the pressure. At constant temperature, taking into account incompressibility of water, from Eq. (3) one gets that the contribution of some water volume in the reverse micelle pool to the Gibbs free energy of the reverse micelle is equal to the product of this volume by the pressure in the water pool. As the water volume V in the micelle water pool is replaced by the same volume occupied by the particle transferred from the water reservoir, the Gibbs free energy of water is changed by $-PV$, and the Gibbs free energy of the particle changes by PV; therefore, the total Gibbs free energy remains unchanged. Thus, the Gibbs free energy of the system has a constant value on going from step (*1*) to step (*2*) and from step (*4*) to step (*5*). Summation of the changes in the Gibbs free energy in all steps gives Eq. (2).

Now we will determine the change in the Gibbs free energy ΔG_{mic} of the micelles. Assume that the particles start to grow in the micelles whose size corresponds to the molar ratio W_0 and that the number of particles is much smaller than that of micelles. The growing particles cause the micelle hosts to "stretch". This leads to a bimodal micelle size distribution (Fig. 2), namely, some micelles have the size corresponding to the molar ratio W_0 while the size of other micelles corresponds to a some larger W value: $W > W_0$. For brevity, we will call the reverse micelles corresponding to the molar ratios W_0 and W "small" and "large" micelles, respectively.

Now a small proportion of water and surfactant molecules from small micelles should be consumed to form large micelles. The corresponding change in the Gibbs free energy is given by

$$\Delta G_{\text{mic}} = N_{\text{S}}\Delta\mu_{\text{S}} + N_{\text{H}_2\text{O}}\Delta\mu_{\text{H}_2\text{O}}, \tag{4}$$

where $N_{\text{H}_2\text{O}}$ and N_{S} are respectively the numbers of the water and surfactant molecules used to form large reverse micelles; $\Delta\mu_{\text{H}_2\text{O}}$ and $\Delta\mu_{\text{S}}$ are the changes in the chemical potentials of water and surfactant upon an increase in the molar ratio from W_0 to W, respectively. Since large micelles are formed using a small proportion of water and surfactant molecules from small micelles, the molar ratio for the small micelles can be considered constant and, therefore, the chemical potentials of the constituent water and surfactant molecules are also constant. The changes in the chemical potentials of water and surfactant are as follows:

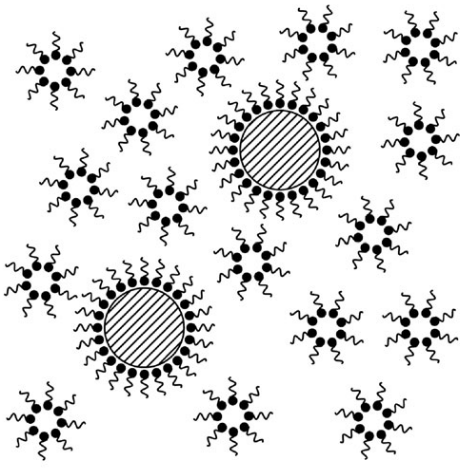

Fig. 2. Bimodal size distribution of reverse micelles appeared in the course of particle growth. The growing particles in the large micelles are dashed.

$$\Delta\mu_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O}}(W) - \mu_{\text{H}_2\text{O}}(W_0), \tag{5}$$

$$\Delta\mu_{\text{S}} = \mu_{\text{S}}(W) - \mu_{\text{S}}(W_0), \tag{6}$$

where $\mu_{\text{H}_2\text{O}}(W)$ and $\mu_{\text{S}}(W)$ are the dependences of the chemical potentials of water and surfactant on the molar ratio W, respectively. The Gibbs—Duhem relation for the reverse micelle solution has the form

$$N_{\text{H}_2\text{O}}\text{d}\mu_{\text{H}_2\text{O}} + N_{\text{S}}\text{d}\mu_{\text{S}} + N_{\text{solv}}\text{d}\mu_{\text{solv}} = 0, \tag{7}$$

where N_{solv} is the number of solvent molecules and μ_{solv} is the chemical potential of the solvent. Since the micelle aggregation numbers are large, the change in the chemical potential of the solvent in Eq. (7) can be neglected; thus one gets

$$N_{\text{H}_2\text{O}}\text{d}\mu_{\text{H}_2\text{O}} + N_{\text{S}}\text{d}\mu_{\text{S}} = 0. \tag{8}$$

Indeed, the differentials $\text{d}\mu_{\text{H}_2\text{O}}$ and $\text{d}\mu_{\text{S}}$ in Eq. (7) are of the order of $kT\text{d}N_{\text{H}_2\text{O}}/N_{\text{H}_2\text{O}}$ and $kR\text{d}N_{\text{S}}/N_{\text{S}}$ respectively, while the differential of the chemical potential of the solvent, in accordance with the theory of dilute solutions, is equal to $kT\text{d}N_{\text{mic}}/N_{\text{solv}}$ (N_{mic} is the number of reverse micelles). Given that at large aggregation numbers, the number of reverse micelle is much smaller than the number of water and surfactant molecules, the last term in Eq. (7) can be neglected.

From the definition of the molar ratio W one has:

$$W = \frac{N_{\text{H}_2\text{O}}}{N_{\text{S}}}. \tag{9}$$

Equations (8) and (9) allow one to express one chemical potential through the other:

$$\mu_{\text{S}} = -\int W\text{d}\mu_{\text{H}_2\text{O}} = -\int W\text{d}\mu'_{\text{H}_2\text{O}}(W)\text{d}W, \tag{10}$$

$$\mu_{\text{H}_2\text{O}} = -\int \frac{1}{W}\text{d}\mu_{\text{S}} = -\int \frac{1}{W}\mu'_{\text{S}}(W)\text{d}W. \tag{11}$$

Taking into account Eq. (11), the change in the chemical potential of water is given by:

$$\Delta\mu_{\text{H}_2\text{O}} = -\int_{W_0}^{W} \frac{1}{W}\mu'_{\text{S}}(W)\text{d}W. \tag{12}$$

From Eqs (4), (6), (9), and (12) one may find the expression for the change in the Gibbs free energy of the system of reverse micelles:

$$\Delta G_{\text{mic}} = \frac{N_{\text{H}_2\text{O}}}{W}(\mu_{\text{S}}(W) - \mu_{\text{S}}(W_0)) - \\ - N_{\text{H}_2\text{O}} \int\limits_{W_0}^{W} \frac{1}{W} \mu'_{\text{S}}(W)\text{d}W. \qquad (13)$$

The change in the surface energy of particles is described by

$$\Delta G_{\text{part}} = (\Omega - \Omega_0)\sigma = \frac{3V\sigma}{R} - \Omega_0\sigma \approx \\ \approx \frac{3\text{v}_{\text{H}_2\text{O}} N_W \sigma}{\frac{3\text{v}_{\text{H}_2\text{O}}}{a_0} W} - \Omega_0\sigma = N_{\text{H}_2\text{O}} \frac{a_0\sigma}{W} - \Omega_0\sigma, \qquad (14)$$

where Ω is the surface area of the particles grown to the size equal to the water pool size of the large micelles; Ω_0 is the surface area of the particles whose size is equal to the pool size of the small micelles; σ is the surface tension of particles; V is the total volume of particles (a constant); R is the radius of the particle; $\text{v}_{\text{H}_2\text{O}}$ is the volume of the water molecule; $\text{v}_{\text{H}_2\text{O}}N_{\text{H}_2\text{O}}$ is the total volume of the large micelle water pools equal to the total volume of particles; and a_0 is the surface area per surfactant molecule on the surface of the reverse micelle. Here we used an approximate expression for the radius of the micelle pool, $R \approx 3\text{v}_{\text{H}_2\text{O}}W/a_0$, which provides a sufficient accuracy for large micelles.

From Eqs (2), (13), and (14), the total change in the Gibbs free energy of particles upon an increase from W_0 to W is

$$\Delta G_{\text{full}} = \frac{N_{\text{H}_2\text{O}}}{W}(\mu_{\text{S}}(W) - \mu_{\text{S}}(W_0)) - \\ - N_{\text{H}_2\text{O}} \int\limits_{W_0}^{W} \frac{1}{W} \mu'_{\text{S}}(W)\text{d}W + N_{\text{H}_2\text{O}} \frac{a_0\sigma}{W} - \Omega_0\sigma. \qquad (15)$$

The particle growth ceases at the molar ratio of large micelles $W = W_{\text{max}}$ corresponding to the minimum in the Gibbs free energy change (15) (Fig. 3), *i.e.*, at

$$\left.\frac{\text{d}\Delta G_{\text{full}}}{\text{d}W}\right|_{W=W_{\text{max}}} = 0. \qquad (16)$$

Bearing in mind that $N_{\text{H}_2\text{O}}$ = const (it follows from the constant total volume of the growing particles), from Eqs (15) and (16) one gets

$$\mu_{\text{S}}(W_0) - \mu_{\text{S}}(W_{\text{max}}) = \sigma a_0. \qquad (17)$$

Equation (17) allows one to calculate the equilibrium particle size using Eq. (1) or to determine that there is no such particle size.

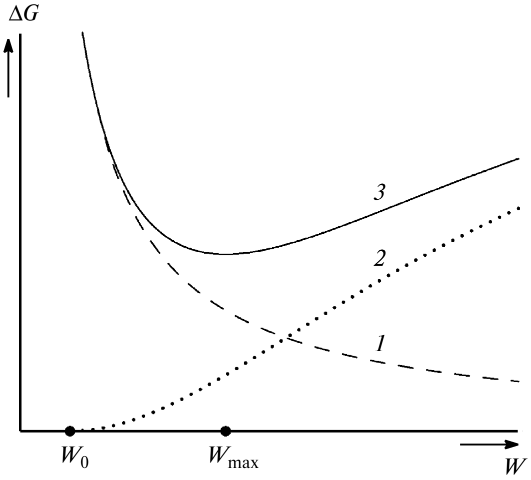

Fig. 3. Qualitative dependences of the changes in the Gibbs free energy on the molar ratio W of large micelles: the surface energy of particles plotted *vs.* W (*1*), the Gibbs free energy of micelle plotted *vs.* W (*2*) and the total change in the Gibbs free energy (*3*).

The dependence $\mu_{\text{S}}(W)$ appeared in Eq. (15) can be obtained from the dependence $\mu_{\text{H}_2\text{O}}(W)$ using Eq. (10). In turn, the chemical potential of water $\mu_{\text{H}_2\text{O}}$ can be determined using the known water vapor pressure under the microemulsion from the expression $\mu_{\text{H}_2\text{O}} = kT\ln(p/p_0)$, where p is the saturation water vapor pressure over the surface of the reverse microemulsion and p_0 is the saturation water vapor pressure over the water surface at the same temperature; the chemical potential of water is calculated relative to pure water. Thus, at the maximum possible parameter W, when the microemulsion can be in equilibrium with the aqueous phase, one has $\mu_{\text{H}_2\text{O}} = 0$. Calculations were carried out using the data[21] for the system AOT—water—isooctane at 37 °C and W values ranging from 0 to 18 (Fig. 4). The dependence of the chemical potential of AOT on the molar ratio W for this system is shown in Fig. 5. The chemical potential of AOT was calculated relative to the state at $W = 50$ (maximum possible

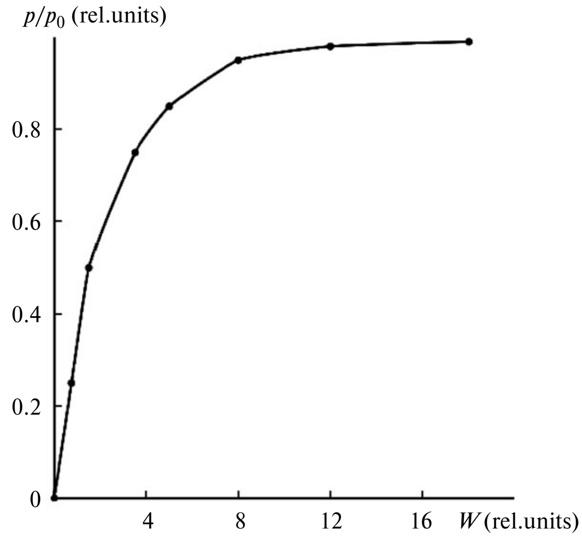

Fig. 4. The saturation water vapor pressure p over the reverse microemulsion AOT—water—isooctane microemulsion at 37 °C plotted *vs.* molar ratio W; p_0 is the saturation water vapor pressure over pure water at the same temperature.[21]

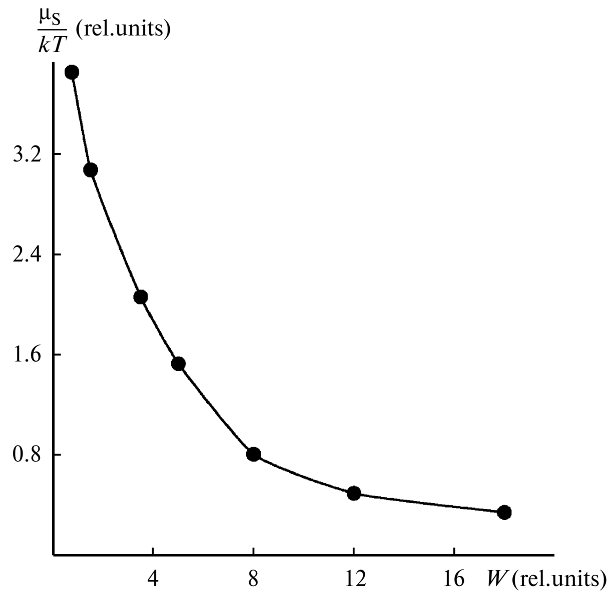

Fig. 5. Plot of the chemical potential of AOT *vs.* molar ratio W calculated using the data of Fig. 3.

W value for this system at 37 °C (see Refs 3 and 22). As the molar ratio W increases from 0.75 to 50, the chemical potential of AOT decreases by $3.9kT$ (see Fig. 5). For the AOT-based reverse micelles, one has $a_0 \approx 63$ Å^2. It follows that Eq. (17) has no solutions at $\sigma > 26$ mJ m^{-2} for the microemulsion in question. The lack of solution means that particle growth cannot be limited. However, inhibition of particle growth is possible at lower surface tension values. In this case, the equilibrium size depends on the surface tension (Fig. 6) and on the molar ratio W_0 (Fig. 7). In the zero surface tension limit, one gets $W_{\max} = W_0$. For any W_0, there exists such a surface tension that at higher surface tension values, particle growth becomes unlimited. *Vice versa*, for each surface tension value, there exists such a W_0 value that at higher W_0 values, the particle growth becomes unrestricted.

Up to this point, our conclusions about the ability of reverse micelle shells to restrict particle growth were based on the water vapor pressure data for a single system. Now we will relate the polydispersity of reverse micelles to their ability to limit particle growth. The relative standard deviation ε_w of the ratio w of the number of water molecules to the number of surfactant molecules in one reverse micelle can be calculated[5] as follows:

$$\varepsilon_w^2 = \frac{kT}{n_S W^2 \frac{d\mu_{H_2O}}{dW}}, \qquad (18)$$

where n_S is the number of surfactant molecules in the reverse micelle. For high molar ratios, the micelle radius can be considered proportional to W and the relative standard deviation ε_r of the micelle radius is approximately equal to ε_w. Taking into account Eqs (8), (9), and (18) one can write

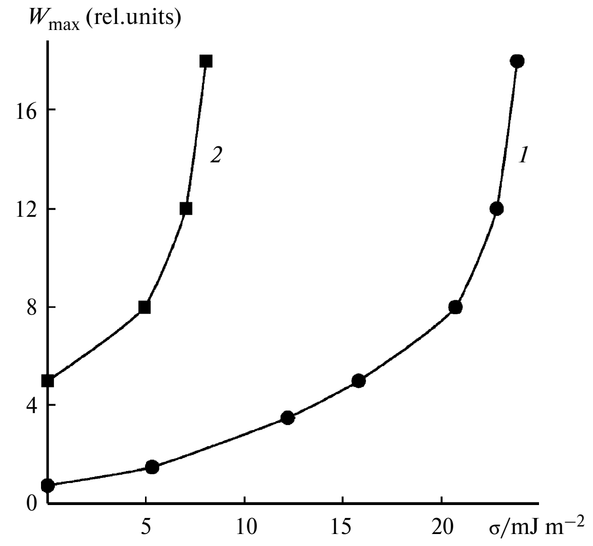

Fig. 6. The equilibrium molar ratio $W_{\max}$ of large micelles in the bimodal size distribution plotted *vs.* surface tension σ of particles for the molar ratios W_0 equal to 0.75 (*1*) and 5 (*2*).

$$\varepsilon_r^2 = \frac{kT}{n_{H_2O} \frac{d\mu_S}{dW}}, \qquad (19)$$

where n_{H_2O} is the number of water molecules in the reverse micelle. The estimate for the chemical potential difference in Eq. (17) has the form

$$\Delta\mu_S \sim W \frac{d\mu_S}{dW} = \frac{n_{H_2O}}{n_S} \frac{kT}{n_{H_2O}\varepsilon_r^2} = \frac{kT}{n_S \varepsilon_r^2}. \qquad (20)$$

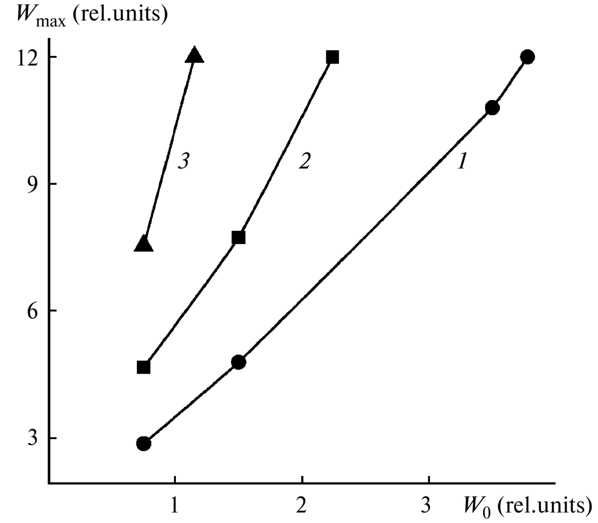

Fig. 7. The equilibrium molar ratio $W_{\max}$ of large micelles in the bimodal size distribution plotted *vs.* molar ratio W_0 for σ equal to 10 (*1*), 15 (*2*), and 20 mJ m^{-2} (*3*).

Substituting the chemical potential difference (20) into Eq. (17), one gets the limiting surface tension above which the particle growth is unrestricted:

$$\sigma \approx \frac{kT}{n_S \varepsilon_r^2 a_0}. \qquad (21)$$

Evaluation for AOT reverse micelles using expression (21) at $W = 0$, $\varepsilon_r \approx 10\%$, and $n_S = 22$ (see Ref. 23) gives a value of 30 mJ m^{-2}. This is consistent with the more rigorous estimate (see above) obtained from the water vapor pressure data. From the estimate (21) it follows that at large W_0 (n_S is also large), particle growth cannot be restricted because otherwise, the surface tension of particles should be too low. The relation to the polydispersity of micelles is not accidental because the decrease in the Gibbs free energy with an increase in the particle size should be compensated by an increase in the Gibbs free energy due to deviation of the micelle size distribution from the equilibrium distribution. In turn, the polydispersity of reverse micelles is related to the so-called rigidity of micelle shells (κ) as follows[5]

$$\varepsilon_r = \sqrt{\frac{kT}{48\pi\kappa\left(1 - \frac{2}{3}\frac{R_0}{R_S}\right) + 6S_0}}, \qquad (22)$$

where R_0 is the average radius of the reverse micelle water pool; R_S is the equilibrium radius of curvature of the micelle shell; and S_0 is a correction including translational motion of micelles in solution. The micelle shell rigidity characterizes the dependence of the Gibbs free energy on the curvature of the shell. Taking into account Eq. (22), the estimate (21) takes the form:

$$n_S a_0 \sigma \approx 48\pi\kappa. \qquad (23)$$

According to expression (23), the ability of reverse micelles to restrict the particle growth is also related to the micelle shell rigidity; this is intuitively understandable.

In the present study, we considered the thermodynamics of restriction of nanoparticle growth by the shells of reverse micelles. Evaluation was performed for AOT because this surfactant is most widely used in the synthesis of nanoparticles in reverse microemulsions. It was found that at typical surface tension values (30 mJ m^{-2} and higher), the reverse micelle shells can not inhibit the particle growth. At lower surface tension values, the particle growth can be restricted at a fairly small molar ratio W_0. In this case, the final particles will be much larger than the initial micelles. At molar ratios larger than 10, particle growth becomes almost unrestricted. Note that when particle grow by consuming individual molecules produced in a chemical reaction, a much higher energy is released compared to particle growth at the expense of the surface energy. Therefore, in the former case, particle growth will be all the more unrestricted. Thus, traditional explanation for the dependence of the size of synthesized nanoparticles on the size of reverse micelles, namely, "the shells of reverse micelles restrict the particle growth", is incorrect. Probably, restriction of particle growth in reverse microemulsions is first of all due to the adsorption of surfactants on their surfaces.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00726-a) and the Ministry of Education and Science of the Russian Federation (Federal Target Program "Scientific and Teaching Staff of Innovative Russia, Years 2009—2013", No. P673).

References

1. M. Kotlarchyk, S. H. Chen, J. S. Huang, *J. Phys. Chem.*, 1982, **86**, 3273.
2. A. V. Nevidimov, V. F. Razumov, *Mol. Phys.*, 2009, **107**, 2169.
3. P. D. I. Fletcher, A. M. Howe, B. H. Robinson, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 985.
4. J. Rička, M. Borkovec, U. Hofmeier, *J. Chem. Phys.*, 1991, **94**, 8503.
5. S. A. Tovstun, V. F. Razumov, *J. Colloid Interface Sci.*, 2010, **351**, 485.
6. J. Eastoe, M. J. Hollamby, L. Hudson, *Adv. Colloid Interface Sci.*, 2006, **128**, 5.
7. V. Pillai, P. Kumar, M. J. Hou, P. Ayyub, D. O. Shah, *Adv. Colloid Interface Sci.*, 1995, **55**, 241.
8. P. S. Khiew, S. Radiman, N. M. Huang, Md. Soot Ahmad, *J. Crystal Growth*, 2003, **254**, 235.
9. K. Holmberg, *J. Colloid Interface Sci.*, 2004, **274**, 355.
10. V. Uskoković, M. Drofenik, *Adv. Colloid Interface Sci.*, 2007, **133**, 23.
11. M. Gobe, K. Kon-No, K. Kandori, A. Kitahara, *J. Colloid Interface Sci.*, 1983, **93**, 293.
12. K. Kandori, K. Kon-No, A. Kitahara, *J. Colloid Interface Sci.*, 1987, **115**, 579.
13. P. Ayyub, A. N. Maitra, D. O. Shah, *Physica C*, 1990, **168**, 571.
14. V. Chhabra, V. Pillai, B. K. Mishra, A. Morrone, D. O. Shah, *Langmuir*, 1995, **11**, 3307.
15. Ph. Monnoyer, A. Fonseca, J. B. Nagy, *Colloids Surf., A*, 1995, **100**, 233.
16. R. Hua, C. Zang, C. Shao, D. Xie, C. Shi, *Nanotechnol.*, 2003, **14**, 588.
17. M. Dvolaitzky, R. Ober, C. Taupin, R. Anthore, X. Auvray, C. Petipas, C. Williams, *J. Dispersion Sci. Technol.*, 1983, **4**, 29.
18. J. Schmidt, C. Guesdon, R. Schomäcker, *J. Nanopart. Res.*, 1999, **1**, 267.
19. M. L. Curri, A. Agostiano, L. Manna, M. D. Monica, M. Catalano, L. Chiavarone, V. Spagnolo, M. Lugarà, *J. Phys. Chem. B*, 2000, **104**, 8391.
20. Y. D. Yan, J. H. R. Clarke, *J. Chem. Phys.*, 1990, **93**, 4501.
21. M. Ueda, Z. A. Schelly, *Langmuir*, 1988, **4**, 653.
22. A. Maitra, A. Sarangi, *J. Biosci.*, 1986, **10**, 403.
23. M. Kotlarchyk, J. S. Huang, S. H. Chen, *J. Phys. Chem.*, 1985, **89**, 4382.

Received March 4, 2011