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Preparation of nanoparticles in reverse microemulsions

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Contents

I.	Introduction	953
II.	General characterization of the method	954
III.	Experimental data	955
IV.	Theoretical concepts	959
V.	Computer simulations	964
VI.	Conclusion	965

Abstract. Experimental data and results of theoretical studies dealing with the synthesis of nanoparticles by the condensation of products of chemical reactions in reverse microemulsions are generalized. Attention is focused on the analysis of mechanisms of nanoparticle nucleation and growth. The bibliography includes 252 references.

I. Introduction

Nanoparticles of different substances with the desired shape, average size and polydispersity are used in different fields of science and technology. As a rule, scientists try to obtain monodispersed particles. The classical synthesis of nanoparticles includes condensation of the product of a chemical reaction carried out in an aqueous medium. However, this method resulted most often in too coarse and polydispersed particles of irregular shape, which was mainly due to coagulation. One of the methods aimed to eliminate these shortcomings is to carry out the reaction in an aqueous pseudophase of a reverse microemulsion.

A reverse microemulsion of the 'water-in-oil' type represents a thermodynamically stable microheterogeneous system consisting of reverse micelles (nanosized water droplets coated by a surfactant monolayer) in a non-polar liquid (oil).[1,2] In place of water, various polar solvents, for instance, alcohols, can be used. Hydrocarbons are the most frequently used non-polar liquids; however, supercritical carbon dioxide was also employed.[3,4] Table 1 shows the typical surfactants required for the preparation of reverse microemulsions.

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The surfactant monolayer on the reverse micelle surface is often considered as its shell, while the water droplet inside a reverse micelle is called its water pool, bearing in mind its relatively isolated position with respect to other water droplets. Due to the Brownian motion, the reverse micelles collide with one another from time to time and form dimers with certain probability; the latter can later dissociate. This process of fusion – dissociation of reverse micelles results in the exchange of the contents of their water pools and is referred to as the intermicellar exchange. Owing to the intermicellar exchange, the totality of reverse micelle water pools can be considered as a common aqueous pseudophase.

The idea of using reverse microemulsions for the synthesis of nanoparticles with the desired geometrical characteristics relied on the assumption that the nanoparticle size is limited by the reverse micelle shells in which the nanoparticles grow. Insofar as the reverse micelles themselves were considered as monodisperse (although this was not exactly the case),[5] it was expected that the nanoparticles prepared in them should also be monodisperse. Moreover, in line with this reasoning, the size of synthesized nanoparticles could be easily varied by changing the water and surfactant concentrations, because the water pool radius of a spherical reverse micelle increases with increase in the water-to-surfactant concentration ratio (W).[6]

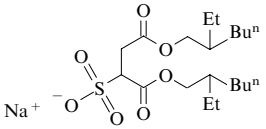
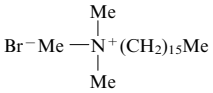
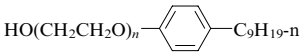
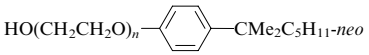
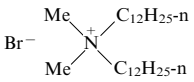
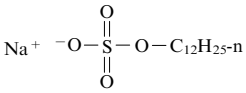
Spherical micelles are used most often; however, other shapes are possible. In the latter case, in line with the idea outlined above, it is expected that the synthesized particles can also be non-spherical.

To select the method for preparation of nanoparticles, particularly, to decide in favour of the reverse microemulsion synthesis and choose the model to be used as the guide in designing the experiment, one must answer the following questions.

— Does this method provide the possibility of preparing monodisperse nanoparticles with the fixed size?

— Is this method suitable for synthesizing nanoparticles of different classes of substances?

Table 1. Surfactants conventionally used in the synthesis of nanoparticles in reverse emulsions.

Formula	Full name	Short name or abbreviation
	sodium bis(2-ethylhexyl)sulfosuccinate	Aerosol OT, AOT
$HO(CH_2CH_2O)_i(CH_2)_{(i-1)}Me$	polyethylene glycol mono-n-alkyl ether	C_iE_j
	cetyl trimethylammonium bromide	CTAB
	polyethylene glycol mono-nonylphenyl ether	NP-n
 (on average, $n = 9.5$)	polyethylene glycol mono-*p*-(1,1,3,3-tetramethylbutyl)-phenyl ether	TX-100, Triton X-100
	didodecyldimethylammonium bromide	DDAB
	sodium dodecyl sulfate	SDS

— Is the growth of nanoparticles limited by the shells of reverse micelles?

— Are there any models capable of describing the growth of nanoparticles in reverse microemulsions?

The available reviews [7–23] of the methods for nanoparticle synthesis in reverse microemulsions fail to give comprehensive answers to these questions. At the same time, a lot of papers (~10 000, according to the data of the search engine scholar.google.com) have appeared after the publication of the first study [24] in this field in 1982. The analysis of the material presented in these papers will help us to answer the questions posed above.

II. General characterization of the method

1. History of development

As indicated in several studies,[16, 19, 24] the method of synthesis of nanoparticles in reverse microemulsions was proposed in the mid-1970s by Friberg and Gault.† In a study dealing with the catalytic hydrogenation of hexene,[26] nanoparticles with a very narrow size distribution were prepared by the reduction of a platinum salt in reverse microemulsions. In 1981, a patent application for the new synthetic method was filed. In 1982, the first detailed description of this method was published.[24] The authors prepared Pt, Pd, Rh and Ir nanoparticles with sizes of 3–5 nm and polydispersity of 10% by the reduction of H_2PtCl_6, $RhCl_3$, $PdCl_2$ and $IrCl_3$ dissolved in pools of reverse microemulsions. As the reducing agents, hydrazine and hydrogen were used. Later (in the period from 1982 to 1986), several publications of other authors [27–35] devoted to the synthesis of nanoparticles in reverse microemulsions appeared. Some of these studies did not refer to the earlier publications;[24–26] hence, some of these authors could have invented this method independently

Initially, it was assumed that each reverse micelle gives rise to a single particle and that the whole amount of reagent contained in its water pool is consumed for the particle growth.[36] The intermicellar exchange was ignored, and micelles were considered as monodisperse. In line with these concepts, the synthesis of nanoparticles in reverse microemulsions would have serious advantages over the methods of synthesis in usual solutions. First, the small size of micelles would allow fine particles to be obtained, because their pools contain small amounts of reagents for their growth. Second, the pool size could be easily regulated by changing the water-to-surfactant concentration ratio. Third, the monodispersity of micelles implies the monodispersity of nanoparticles synthesized in them.[26, 30, 36]

However, the authors of this method soon became aware that this concept is wrong. Thus they wrote [24] that it appears attractive to assume that each particle is formed from a single reverse micelle. However, in the further text they pointed out that the size assessed under this assumption was much smaller that that observed experimentally.

† Gault worked in the University of Strasburg (France) where he studied the catalysis of hydrocarbon isomerization and hydrogenation by metal nanoparticles. In 1976, he visited Friberg, who worked in the Institute of Surface Chemistry (Sweden) and told him that he needed a method for synthesizing nanosized particles for catalysis. Friberg dealt with reverse microemulsions and proposed to use the latter in the synthesis of nanoparticles. A short time later, Friberg left for the USA and Gault died. As the result, they published no papers on the synthesis of nanoparticles in reverse microemulsions. Boutonnet, a co-worker of Gault [25, 26] used this method for synthesizing nanoparticles.

To correctly describe the growth of nanoparticles in reverse micelles, one should take into account the intermicellar exchange, which means that reactants from many micelles are involved in the formation of a single particle. Thus, this method appeared on the *a priori* incorrect basis which ignored the intermicellar exchange; however, the particles synthesized in this way were indeed smaller and more uniform than those prepared in usual aqueous solutions.

The efficiency of this method was once again explained in the early 1990s and many scientists still hold to the proposed explanation. This states that the particle size is limited by the size of micelles in which the particles are synthesized because the surfactant monolayer at the pool boundary prevents the particles from growing. Probably, this idea was first formulated in 1987 in a study by Fendler.[7]

2. Different versions of this method

There are several versions of the synthesis of nanoparticles in microemulsions differing in the procedure of introduction of the required reactants. The most widely used version consists of blending of two microemulsions with the reactants dissolved in their aqueous pseudophases.[30, 31, 37–143] A version according to which the reverse micelles in solutions to be mixed contain no water but include solubilized reactants necessary for the synthesis of nanoparticles is also possible.[144] In the frequently used method, a microemulsion containing one of the reactants is mixed with a solution of the other reactant in water or oil (Refs 24, 30, 32, 34, 36, 53, 65, 99, 109, 145–179). With such procedure of mixing, a stable single-phase microemulsion is not necessarily formed; however, sometimes, particles with sufficiently narrow size distributions are synthesized.[180, 181] Often, one of the reactants is dissolved in the aqueous pseudophase of microemulsion, while the second reactant is bubbled through as a gas.[24, 27, 33, 36, 48, 182–187]

In certain cases, all reactants are solubilized in one microemulsion and the reaction is stimulated by electromagnetic radiation[28, 29, 53, 151, 188] or heating.[189–191] All reactants can also be solubilized in one microemulsion provided the reaction time is shorter than the mixing time.[179, 192–195]

Sometimes the use of reverse micelles for synthesizing nanoparticles does not involve carrying out any chemical reactions in them. Thus, solubilization of solids in the polar cores of anhydrous reverse micelles may result in solid dispersion to form nanoparticles.[196–201] Solutions of reverse micelles can also be used as a medium for transferring reactants from one solid phase to another and also for dispersing the reaction product formed.[202]

The following procedures of reactant mixing are used: pouring of one microemulsion into the other at a constant rate,[203–207] slow pouring of a reactant or its solution into a microemulsion,[120, 208] pouring of two aqueous solutions into a microemulsion,[209] slow pouring of two microemultions into the third one.[210–212]

If the synthesis of nanoparticles involves a metal ion, then a solution of its salt is conventionally used in the preparation of a microemulsion containing this metal. However, another method exists in which the microemulsion is prepared using an ionic surfactant with the counter ion taking part in the reaction.[45] For example, such surfactant can be prepared by substituting a given metal ion for the sodium ion in AOT.

3. Chemical composition of particles synthesized in reverse microemulsions

Reverse microemulsions are mainly used to synthesize inorganic nanoparticles, namely, salts, metals, oxides. Salt nanoparticles are most often prepared by ion exchange reactions. For instance, cadmium sulfate nanoparticles can be formed upon mixing of microemulsions one of which contains solubilized cadmium nitrate and the other contains sodium sulfide

$$Cd(NO_3)_2 + Na_2S \longrightarrow CdS + 2\,NaNO_3\,.$$

Metal nanoparticles are synthesized *via* the reduction of their compounds by means of radiolysis, under the action of sodium borohydride, hydrazine, sodium metal,[53] *etc*. For instance, gold particles are often prepared by the reduction of chloroauric acid; silver nanoparticles were obtained by the reduction of silver nitrate. Oxides TiO_2 and SiO_2 were synthesized by the hydrolysis of $Ti(OBu^n)_4$ and $Si(OC_2H_5)_4$, respectively.

Sometimes, the particles synthesized in reverse microemulsions are not the final product and have to be subjected to additional treatment. For example, ferromagnets ($BaF_{12}O_{19}$, $CoFe_2O_4$), high-temperature superconductors ($YBa_2Cu_3O_{7-x}$, BiPbSrCaCuO) and catalysts (TiO_2) were synthesized by annealing nanoparticles of the corresponding metal oxalates, carbonates or hydroxides synthesized in reverse micelles.

Nanoparticles of organic compounds are rarely synthesized in reverse micelles. This way the nanoparticles of latex,[28, 35] cholesterol, vanilline (4-hydroxy-3-methoxybenzaldehyde) and ethylvanilline (4-hydroxy-3-ethoxybenzaldehyde),[200, 213] J-aggregates of cyanine dyes[214] were synthesized.

As a rule, the choice of synthesized substances is determined by the prospects of their practical use. Originally, the nanoparticles were synthesized in reverse micelles to be used as catalysts. The synthesis in reverse micelles makes it possible to obtain sufficiently fine particles with large surface-to-volume ratios, which is the factor important for assessing the catalyst efficiency. The representative materials for catalysis synthesized in reverse microemulsions are as follows: nickel boride[32] (catalyst of hydrogenation of unsaturated hdyrocarbons), iron[53] (catalyst of ammonia synthesis, the Fischer–Tropsch process, *i.e*., synthesis gas transformation to liquid hydrocarbons), cadmium sulfide and titanium oxide (catalysis of photochemical reactions under irradiation with light, particularly, the reaction of water decomposition). Furthermore, mixed oxides and salts were synthesized in reverse microemulsions. The synthesis in micelles allowed the components to be efficiently mixed on the nanoscale level. High-temperature superconductors[46, 54, 62] and ferrites[111, 173] were prepared in this way. The latter were used in devices for magnetic storage of information. Table 2 shows the substances synthesized most often in reverse microemulsions.

III. Experimental data

1. Correlation between the sizes of nanoparticles and micelles

The authors of many studies assumed the particle size to be limited by the size of micelle pools in which they were grown (Refs 13, 46, 47, 50, 54, 56, 62, 64, 80, 82, 107, 115, 118, 141, 150, 174, 205, 215–218). However, some scientists did not

Table 2. Nanoparticles synthesized most often in reverse microemulsions.

Substance	l (%) [a]	Ref.	Substance	l (%) [a]	Ref.
CdS	15 – 22	33, 37 – 40, 45, 43, 48, 52, 53, **63**	Ag	39	**49**
	9.5 – 12	64, 66, 78, **98**		44	53, **61**
	15 – 20	**100**		43	**83**
	25	112, 115, 123, **127**		29 – 107	**101**
	12 – 18	139, 141, 185, 189, **194**		37	**119**
	24	195, **205**		33	**124**
	–	206		31 – 37	**134**
Au	14 – 28	29, 53, **57**		40	**148**
	15	75, 76, **99**	AgBr	30	41, 44, **51**
	13 – 37	**109**		11 – 38	**69**
	28	111, 113, 129, 133, **143**		45 – 60	79, 89, 105, 116 – 118, **172**
	40	**148**		34 – 63	**178**
	5 – 20	**151**	TiO_2	8.2 – 169	73, 192, 152, 159, 168, 170, 179, 193, **208**
	6 – 32	188, **207**	$BaSO_4$	–	77, 84, 86, 96, 102, 125
Cu	10 – 50	**55**, **58**	CdSe	25	**146**
	9 – 39	**63**		9 – 15	**174**
	10 – 34	119, **153**		–	177, 191, 206
	10 – 30	**154**	SiO_2	4	**65**
	12	**156**		8.5	**147**
	11 – 31	**160**		4.5 – 11.5	**161**
	–	163, 164, 166		3 – 33	165, **175**
Pd	13	24, 36, 53, 74, **93**	Ag_2S	30	47, 123, **155**
	23	99, **107**		28	158, **171**
	9.3 – 23	**132**	PbS	22	38, 60, 71, 87, **205**
	7.1 – 23	145, **203**	AgI	–	47, 79, 104, 114, 118, 130, 142
	11	**204**	$CaCO_3$	22	86, 131, **182**
Pt	10	**24**, **36**		18 – 34	**183**
	11 – 13	53, **57**		15	**184**
	18	94, 110, **124**	ZnS	–	64, 66, 90, 92
	10	**145**	Rh	–	24, 36, 53, 145
	38	**149**	Fe_3O_4	6.1 – 12	30, 111, **173**
AgCl	19 – 32	31, 47, 79, **88**	Co	25 – 40	**153**
	40 – 55	117, 118, **120**		–	157
	18.3	210, **211**	BaF_2	–	121, 128
	–	212	CuS	–	38

Note. The shown values of parameter l were taken from references shown in bold face; dash corresponds to the absence of size distribution in the cited study. [a] l is the relative width of the size distribution for synthesized nanoparticles.

share this opinion [31, 121, 203, 219] and some experimental data revealed that this is not the case.[81, 100] In certain cases, it was observed [61] that the micelle size can only indirectly affect the particle size, *i.e.*, the micelles restricted the particle growth by limiting the aggregation (for small W ratios). The majority of authors pointed out that the particle size is 'controlled' by the micelle pool size, implying that the size of synthesized particles is a function of the pool size but need not be equal to the latter. Then, the term 'control' should be considered as a poor choice and even misleading because it infers that the particle size is a function of only the pool size, which is not true in many cases.

To check the correctness of this assumption, we plotted a diagram (Fig. 1) that reflects the relationship between the diameters of pools and particles for AOT-based micelles, because AOT is the only surfactant for which the relationship between W and the pool diameter (nm) was revealed with a sufficient degree of reliability:

$$d_p = 0.35W + 1.$$

This formula was written based on the experimental data [6] by taking into account the fact that the micellar shell thickness was ~ 1 nm.[220]

The linear dependence of the reverse micelle water pool diameter on the molar ratio W was derived based on the following geometrical reasoning. The reverse micelle core volume is the sum of volumes of water and surfactant polar groups

$$\frac{\pi}{6} d_p^3 = N_a V_a + N_s V_s, \quad (1)$$

where d_p is the water pool diameter; N_a, N_s are the numbers of water and surfactant molecules in a reverse micelle; V_a and V_s are the volumes of water molecules and surfactant polar groups in a reverse micelle. The pool surface in a reverse micelle is

$$\pi d_p^2 = N_s a_0, \quad (2)$$

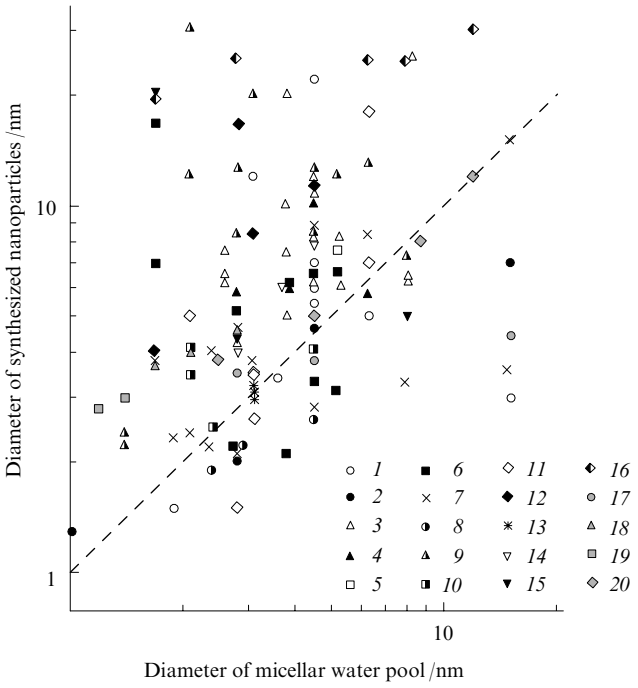


Figure 1. Correlation between the diameters of water pools in reverse micelles and the diameters of particles synthesized in these micelles for AOT-based microemulsions.
Dashed line corresponds to the case where the water pool and the particle have equal sizes. (*1*) Ag,[83, 101, 119, 124, 134, 155, 158] (*2*) Ag_2S,[123, 155, 158] (*3*) AgBr,[44, 51, 69] (*4*) AgCl,[31, 88] (*5*) AgI,[142] (*6*) Au,[57, 207] (*7*) CdS,[39, 45, 48, 52, 64, 78, 98, 123, 127, 139, 141] (*8*) CdSe,[146, 174] (*9*) Cu,[55, 58, 156, 166, 119] (*10*) PbS,[71, 87] (*11*) Pd,[74, 93, 132] (*12*) Pt,[57, 94, 124] (*13*) ZnS,[64, 90, 92] (*14*) Co_2B,[85] (*15*) GeO_2,[91] (*16*) $CaSO_4$,[96] (*17*) CdTe,[106] (*18*) CuO,[176] (*19*) PbI_2,[140] (*20*) Fe.[59]

micelle distribution deviates from the equilibrium one, *i.e.*, in addition to micelles with the original diameter, the micelles of larger diameters accommodating growing particles appear. This leads to the increase in the Gibbs free energy of reverse micelles. In turn, as the particles grow, the thermodynamic potential of the system, *i.e.*, the totality of micelles with a particle inside, decreases. The growth should stop when the particle size corresponding to the minimum of the free energy of the system is reached (Fig. 2). For the growth of particles due to a decrease in their total surface, *e.g.*, for Ostwald ripening and coagulation, it can be shown[221] that the particle size corresponding to the mini-

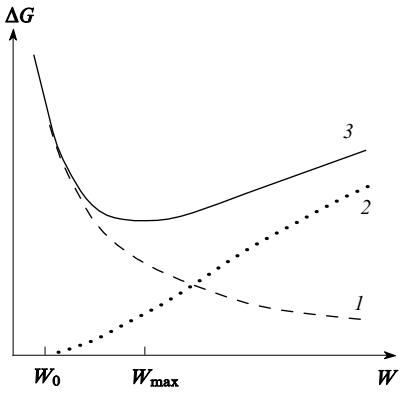


Figure 2. Qualitative illustration of the change in the Gibbs free energy *vs.* the molar ratio W typical of coarse micelles;
(*1*) the decrease in the thermodynamic potential of the system due to the particle growth, (*2*) the dependence of the thermodynamic potential of micelles on W, (*3*) the total change in the thermodynamic potential.

where a_0 is the area one surfactant molecule occupies on the reverse micelle surface. Division of Eqn (1) by Eqn (2) gives

$$d_p = \frac{6V_a}{a_0} W + \frac{6V_s}{a_0},$$

where

$$W = \frac{N_a}{N_s}.$$

In the majority of cases, the average diameter of synthesized particles differed from the pool diameter by more than 50% (see Fig. 1).

The inability of a micelle to stop the growth of the particle inside it is indirectly confirmed by the fact that the microemulsion as such is often even incapable of solubilizing quite modest amounts of salts necessary for synthesis, because the size, position and shape of the microemulsion stability domain in its phase diagram depend strongly on the concentrations of salts in the aqueous pseudophase.[69] This is why the question of whether reverse micelles are sufficiently stable to restrict the particle growth is open.

Indeed, once the particle size reaches the pool size, its further growth is hampered by the micellar shell. Insofar as the micellar cores are not absolutely rigid, then under the pressure of particles growing inside reverse micelles, the latter should increase in size by exchanging water and surfactant molecules with other micelles. As a result, the mum of the free energy can be found from the following equation:

$$\mu_s(W_0) - \mu_s(W_{max}) = \sigma a_0, \quad (3)$$

where $\mu_s(W)$ is the chemical potential of the surfactant as a function of the molar ratio W, W_0 is the molar ratio of original micelles with the diameter d_0, W_{max} is the molar ratio of micelles with diameters corresponding to the diameters of particles d, s is the surface tension of particles.

Estimates according to Eqn (3) have shown that for typical values of surface tension (> 30 mJ m^{-2}), the reverse micelles could not limit the particle growth because this equation has no solution. For lower values of surface tension, the limitation is possible; however, the equilibrium size of particles turned out to be much larger than the original micelle size.

Thus, the results of experimental and theoretical studies have shown that the size of nanopartcles in the synthesis in reverse micelles is not limited by the size of reverse micelle pools. However, it was often noted that for all other conditions equal, the size of synthesized nanoparticles increased with the enlargement of reverse micelles. Considering the results of studies referred above, for substances such as Ag_2S, AgBr, Au, CdS, CdSe and ZnS, the increase in the size of synthesized nanoparticles observed with the growth of micelles can be regarded as trustworthy.

2. Kinetics of nanoparticle growth

The kinetics of nanoparticle growth in reverse micelles is still unclear. The so far obtained experimental results are insufficiently accurate; and, hence, it is difficult to find the functional relationships between the particle size and their growth time. These relationships could be helpful when studying the mechanisms of nanoparticle growth. Nonetheless, the experimental data on the growth kinetics can be divided into the following three groups: data obeying the logarithmic and power laws and also data corresponding to the kinetic with cessation of growth. These groups correspond to different mechanisms of growth, which will be considered in detail below (see Section IV). The most important of these mechanisms are the coagulational growth and also the Ostwald ripening in which the coarser particles increase due to dissolution of finer ones. Moreover, the growth can occur either in parallel with chemical reactions supplying the precursors or at a constant total amount of substance formed in a chemical reaction in the initial stage of this process.

Logarithmic kinetics. In several studies,[64, 71, 78, 79, 98, 142] the dependences of the diameter d of CdS, ZnS, PbS, AgI, AgBr particles on the time (t) in the course of growth can be considered as logarithmic

$$d \sim \ln(t + t_0), \tag{4}$$

which may be a result of the coagulational growth mechanism described below. Due to experimental errors, a logarithmic dependence is often difficult to distinguish from a power law dependence

$$d \sim t^n \tag{5}$$

with the exponent n far below unity. For instance, based on the analysis of the growth kinetics of ZnS particles, it was concluded [90, 92] that the latter obeyed the power law dependence with the exponent 0.1. Meanwhile, the same data can be described under the assumption of the logarithmic dependence. From our viewpoint, the logarithmic dependence should be preferred because it admits a simpler interpretation as compared with the power law dependence with a low exponent. The experimental data on the growth kinetics of Cu, $KMnF_3$, CdSe nanoparticles, which was acquired in Refs 11, 166 and 174, respectively, can also be described by similar logarithmic dependences.

Power law kinetics was revealed in our analysis of experimental data on the synthesis of SiO_2, Cu, AgCl particles obtained in several studies.[65, 163, 210] The degree n in the dependence (5) for SiO_2 particles turned out to be 0.3 (Ref. 65), which corresponds to an approximately constant rate of particle volume change. For the growth kinetics of copper nanoparticles, the exponent n proved to be close to 0.5 (Ref. 163). In the synthesis of nanoparticles in reverse micelles based on NP-6, the particle growth rate was often independent on the reactant concentration.[210] This provided conclusion that the growth proceeded due to the Ostwald ripening. For this mechanism, the power law dependence of the particle size on time with the exponent 1/3 should be observed. Within the error, the obtained experimental data well agreed with the mentioned power law dependence; however, for larger numbers of particles, the growth rate was observed to decrease somewhat more quickly.

Kinetics with cessation of growth is characterized by the fact that from a certain moment the growth can be considered as stopped to within the experimental error. This was evidenced by the data on the synthesis of GeO_2,[91] Pd,[93] Pt,[94] Cu and Ag [119] particles.

The kinetics according to which the growth rate of particles is, one or another way, limited by the rate of delivery or formation of precursors can hardly provide sufficient information for the elucidation of the growth mechanism. Thus for the synthesis of CdS nanoparticles,[194] a linear dependence of the particle volume on the time was revealed. This can be explained by an approximately constant rate of thioacetamide decomposition to supply S^{2-} ions needed for the growth of particles. Mention should be made of a study [184] in which the kinetics of growth of $CaCO_3$ particles on CO_2 bubbling through a $Ca(OH)_2$-containing microemulsion was considered. According to this study, the volume of synthesized particles was proportional to the amount of absorbed carbon dioxide.

3. The effect of solvent

The effect of solvent is for the most part reduced to two factors. First, the solvent molecules are incorporated into the micellar shell. It is assumed that for the bulkier solvent molecules, the incorporation into the micellar shell is more difficult and the rate constant for the intermicellar exchange is higher. Second, the nature of solvent determines the van der Waals interactions between particles and micelles. Several publications consider the effect of solvent on the growth of particles for AOT-based microemulsions.

It was shown [43] that the initial stage of growth of CdS nanoparticles is ideally described by the coagulational model in which the rate constant for coagulation was replaced by the rate constant for intermicellar exchange.

Studying the growth kinetics of AgBr nanoparticles in microemulsions in which the oil phase was built by alkanes with chains of different lengths [44] has shown that with the increase in the chain length, the growth process accelerates and the solution instability aggravates. In a microemulsion formed by n-hexane, the particles did not precipitate for at least six weeks. The substitution of n-heptane or n-octane for n-hexane afforded somewhat coarser but still stable particles. With the transition to n-dodecane and n-tetradecane, the flocculation occurred.

It was shown [61] that silver nanoparticles synthesized in cyclohexane were smaller than the particles synthesized in isooctane.

The SiO_2 particles prepared in cyclohexane were found [161] to be finer than particles synthesized in heptane. This can be explained by the higher concentration of cyclohexane molecules in the micellar shell, which resulted in the decrease in the micelle size. This explanation differs from the more widely accepted concept according to which the penetration of solvent molecules into the shell can change the constant of intermicellar exchange.

The effect of the intermicellar exchange rate on the growth of AgCl and Ag particles was studied.[88, 101] Cyclohexane, heptane and decane were used as non-polar media; the corresponding rate constants for intermicellar exchange were 10^6, 10^7 and 10^8 litre mol^{-1} s^{-1}, respectively. The maximum particle size was obtained for heptane. For AgCl, this was attributed to the effect of the exchange rate on the rates of nucleation and growth of particles and for Ag, to the fact that the reaction proceeded incompletely.

Studying the effect of the solvent on the growth of copper nanoparticles revealed [166] that the initial rate was higher in isooctane than in cyclohexane but the final particle size was somewhat higher in cyclohexane. It was found that W affected the growth rate but did not affect the final size of particles. A theory was developed [119] according to which the final particle size was determined by the energy of interaction of particles in solution and this energy depended on the nature of solvent. However, the authors did not clarify the latter statement; maybe they meant the stability of particles against coagulation.

The effect of the nature of solvent and the parameter W on the growth of AgI nanoparticles in reverse AOT micelles was studied.[142] As the solvents, normal alkanes with the chains including 6, 8, 10 and 12 carbon atom were used. The parameter W varied from 2 to 16. For $W = 2$, the growth rate turned out to be independent of solvent, whereas for higher W, the growth rate increased with the alkane elongation.

4. Non-spherical particles

In reverse emulsions, spherical particles are prepared most often. However, in several studies, non-spherical particles were synthesized mainly in the form of rods {$Co_3[Co(CN)_6]_2$,[190] $CaSO_4$,[96] $BaCrO_4$,[97] $BaWO_4$,[222] TiO_2,[179] CdSe,[177, 191, 206] CdS,[206] Au,[99, 109, 129, 188] Cu,[55, 58, 153, 160, 163, 164, 223, 224] Pd (Ref. 99)}, filaments [$CaCO_3$,[131] $BaSO_4$,[84, 102] $CaSO_4$,[96] $CaHPO_4$,[137] $BaCrO_4$ (Ref. 97)], wires [$CePO_4$,[135] $BaCO_3$,[86] AgI (Refs 114, 118)], cubes {LiF,[95] BaF_2,[128] $Co_3[Co(CN)_6]_2$,[190] $KMnF_3$,[111] Cu,[153, 160, 223] Au,[99, 129] Pd (Refs 91, 99)} and lamellar trigonal crystals [Cu,[153, 160, 223] Au,[99, 109, 129] Pd,[99] CdS (Ref. 185)]. Moreover, hexagonal Au crystals,[99] CdSe dendrites,[177] TiO_2 particles shaped as shuttles [168] and dumbbells,[179] lamellar and rhombic $BaSO_4$ crystals,[84] Pb(OH)Cl nanotubes [138] were prepared. The nonsphericity of prepared particles was explained by different factors. The widely accepted explanation was based on the template concept, namely, the shape of particles should repeat the shape of micelles in which they were synthesized. Most often, this concerned elongated particles or rods (see Refs 55, 58, 114, 115 and also 118, 135, 138, 153, 160, 163, 177, 188, 206, 223, 224). Presumably, the appearance of elongated particles in spherical micelles was due to the elongated shape of micellar dimers formed during the intermicellar exchange.[84, 97, 179, 191] There is no sufficient grounds for this explanation and several contradicting examples can be shown.[96] Particularly, within the framework of the template concept, the triangular shape of particles cannot be explained because no triangular micelles are known in the literature.

In their studies, Pileni *et al.* focused attention on the template synthesis. In their early studies,[63, 223] they pointed out that the particle shape is dictated by the micelle shape. In 1998, they applied the template approach to the synthesis of copper nanorods with the use of a functionalized surfactant.[163] For this purpose, microemulsions based on $Cu(AOT)_2$ were chosen.[225–227] However, it was soon shown [164] that templates tend to change with the delivery of reactants or with the consumption of a functionalized surfactant in the course of reaction. The shape of synthesized particles was preferentially determined by the added salts. Later, the fallacy of the earlier conclusions on the role of templates was revealed; in this connection several publications are pointed out.[12, 15, 58, 154, 160, 163, 223, 224] In some reviews (Refs 228 and 229), it was noted that a template is not the only factor that determines the shape of synthesized particles and that the effect of selective adsorption on the faces of growing crystals is much stronger, whereas the role of surfactants is reduced to stabilization of these faces. In yet another study,[230] the authors provided a new explanation to the surfactant role in the synthesis of particles, namely, it was shown that the surfactant can affect the particle growth only when present in solution in its free state capable of adsorption on the crystal faces. For reverse micelles, free surfactant is absent; hence, its influence on the growth is nil.

Thus, the structures of the 'water in oil' type were considered as unsuitable for templates. Nor the structures such as 'oil in water' were suitable, because a substantial role in them was played by poorly controllable impurities which were the source of non-reproducibility of results. This means that the approach to the synthesis of non-spherical particles with the use of reverse micelle-based templates lacks serious grounds. Nonetheless, we cannot totally agree with the above reasoning because the free (unreacted) surfactant is present in both direct and reverse microemulsions.

There were also other reasonable explanations for the nonsphericity of prepared particles, namely, by the directed aggregation [96, 102, 138, 168, 189, 191] and by the growth of crystal faces at different rates [138, 177, 195] determined by the adsorption of surfactants [126, 128] or salt ions [190] on these faces. The crystal shape was also shown to depend on its structure [128] formed in the particle nucleation stage and to be very sensitive to synthetic conditions.

According to a classification,[84] the methods of synthesis of particles of desired shapes with the use of surfactants can be divided into template-oriented syntheses and morphosyntheses. In the former method, the particular surfaces of aggregates of supramolecular surfactants were proposed to be used in modifying the processes of nucleation and growth of particles in certain sites; in the latter method, the structures formed by surfactants were used to limit the particle growth.

IV. Theoretical concepts

The synthesis of nanoparticles in reverse micelles involves processes similar to those involved in the syntheses in homogeneous solutions, namely, chemical reaction, particle nucleation and particle growth. There are several types of particle nucleation and growth processes. If the critical nucleus is so small that represents a single molecule, the nucleation is in fact absent. For a critical nucleus that is not so small, two nucleation modes are possible, which correspond to the instantaneous supersaturation and its slow development (Fig. 3). For the instantaneous supersaturation, the nucleation starts immediately and the growth of the resulting particles leads to a decrease in the supersaturation (Fig. 3 *a*). This, in turn, results in cessation of nucleation, but the growth continues.[231] In the mode of slow development of supersaturation described by the LaMer diagram [232] (Fig. 3 *b*), the supersaturation increases due to some factor (for instance, a chemical reaction or the delivery of reactants to the reactor) upon an increase in the concentration of the monomer from which the particles are formed. As a certain concentration (c_{nucl}) has been reached,

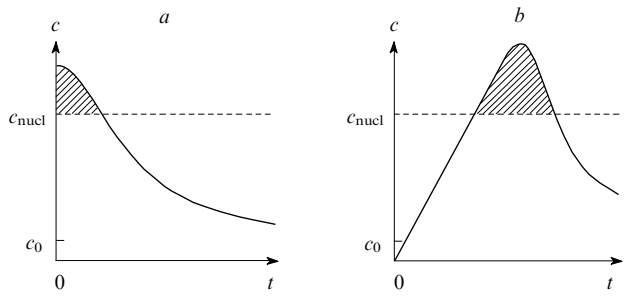


Figure 3. LaMer diagrams for the instantaneous (*a*) and gradual (*b*) modes of the development of supersaturation;
t is time, *c* is concentration, c_{nucl} is concentration above which the nucleation is possible, c_0 is equilibrium concentration; dashed region corresponds to the nucleation domain.

the nucleation begins. As the particles grow, their growth consumes the increasing amounts of supplied monomer, which reduces the supersaturation and, as a consequence, the nucleation ceases. Moreover, as for the instantaneous supersaturation, the particles continue to grow.

The pioneering study [232] described growth through the addition of monomers controlled by the diffusion of the monomer to the particles. However, in the general case, the consideration should not be restricted only to this growth mechanism. The growth through the addition of monomers may be controlled by the stage of their addition to the particle surface. The particles can also grow due to coagulation or Ostwald ripening. Their growth can stop either as a result of depletion of reactants or due to the forced interruption of synthesis.

Sometimes, the growth is observed to slow down, which can be considered as its cessation. Yet another possible version considers the particles of a certain size as thermodynamically stabilized by the adsorbed surfactant so that these particles can neither grow nor dissolve because their total surface is determined by the surfactant amount. For example, it was proposed [200, 213] to describe the synthesis of nanoparticles within the framework of two simplified models. The first model is based on the LaMer diagram and the second one relies on the thermodynamic stabilization of particles. In the former case, the final size of particles should depend on the reactant concentration and the size of micellar water pools. In the second case, the final size of particles should be independent of these parameters.

Thus, the dependence or independence of the particle final size on the concentration is the criterion for the choice of the mechanism in each particular case. Based on this criterion, the growth mechanism of particles can be assigned [200, 213] to either the model based on the LaMer diagram or the model of thermodynamic stabilization. We consider this approach as quite reasonable but insufficiently substantiated. Its authors correctly noted that the possibility of thermodynamic stabilization of particles of a certain size was scarcely discussed in the literature. In essence, this stabilization is the manifestation of the Rehbinder effect [233] considered many years ago, *i.e.*, a decrease in the strength of solids upon adsorption of surfactants. If the adsorption is sufficiently high and dramatically decreases the surface tension of a solid, the solid may spontaneously disperse to form a thermodynamically stable colloid system.

Within the framework of the described scheme of nucleation and growth, at least two types of reactions affording nanoparticles can occur. Generally, the reaction of formation of product (P) molecules, which later aggregate to nanoparticles, is considered

$$\mathrm{A} + \mathrm{B} \longrightarrow \mathrm{P}, \qquad (6)$$
$$n\,\mathrm{P} \longrightarrow \mathrm{P}_n.$$

Thus the metal nanoparticles can be synthesized by the reduction of metals from their salts.

The second reaction type includes, for example, the synthesis of salts from the corresponding ions, where the critical nucleus is formed from two ions

$$n\,\mathrm{A}^{p+} + m\,\mathrm{B}^{q-} \longrightarrow (\mathrm{A}_n\mathrm{B}_m)^{np-mq},$$
$$np \approx mq.$$

The specificity of synthesis in reverse micelles is largely associated with the intermicellar exchange, which modifies the reaction kinetics. Let us consider this by the example of reaction (6) mentioned above. Let reactant A reside in water pools of one microemulsion and reactant B occur in the pools of the other emulsion. The reactants are usually assumed to be randomly distributed over the pools. Upon blending of microemulsions containing reactants A and B, the exchange of the contents of their water pools occurs, which results in their reaction (Fig. 4).[14, 234] If the rate

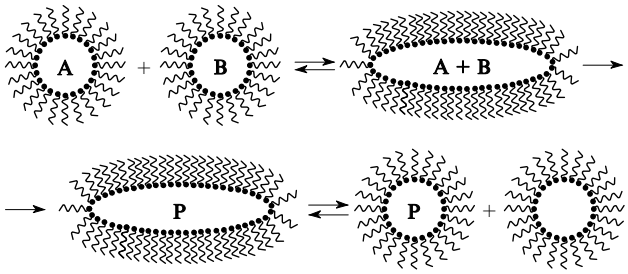


Figure 4. Illustration of intermicellar exchange.

constant of this reaction in aqueous solutions is sufficiently high, then upon blending of the microemulsions, this reaction may become controlled by the intermicellar exchange. Moreover, for a large average number of reactants per micelle, the reaction kinetics proved to be rather complicated.[235, 236] At the same time, for a low rate constant, as assumed in theoretical studies below, the reaction rate depends on the reactant distribution in reverse micelles. However, insofar as the slow reaction does not disturb the equilibrium distribution over micelles, the reaction rate can be assessed by using the mass action law for a homogeneous aqueous solution; from our point of view, this way is easier. Indeed, the reaction rate throughout the microemulsion is equal to the sum of rates in individual micelles

$$\frac{\mathrm{d}c_\mathrm{P}}{\mathrm{d}t} = \frac{1}{Mv}\sum_{n_\mathrm{A}=0}^{\infty}\sum_{n_\mathrm{B}=0}^{\infty} M p_\mathrm{A}(n_\mathrm{A}) p_\mathrm{B}(n_\mathrm{B})\, k\, \frac{n_\mathrm{A}}{v}\frac{n_\mathrm{B}}{v}\, v = \qquad (7)$$
$$= \frac{k}{v^2}\left(\sum_{n_\mathrm{A}=0}^{\infty} p_\mathrm{A}(n_\mathrm{A}) n_\mathrm{A}\right)\left(\sum_{n_\mathrm{B}=0}^{\infty} p_\mathrm{B}(n_\mathrm{B}) n_\mathrm{B}\right) = k c_\mathrm{A} c_\mathrm{B},$$

where c_A, c_B and c_P are the concentrations of molecules A, B and P, respectively, calculated per aqueous pseudophase (expressed in the number of molecules per volume unit); M is the number of micelles; v is the micelle water pool volume, $p_A(n_A)$ and $p_B(n_B)$ are the probabilities that n_A and n_B numbers of reactant molecules A and B, respectively, are localized within the micelle; k is the reaction rate constant in a homogeneous aqueous solution. The double sum means the number of molecules of reactant P formed per unit time; Mv is the volume of the aqueous pseudophase; single sums represent average numbers of A and B molecules per micelle. The effect of the intermicellar exchange on the coagulation rate of particles can be considered in a similar fashion.

The intermicellar exchange can also control the nucleation rate. As a rule, the product P is assumed to be initially dissolved in water pools in the form of molecules or atoms. Once its concentration becomes sufficiently high, the nucleation of the product P solid phase occurs. Usually, the presence of even one molecule of substance P in the reverse micelle pool formally corresponds to its very high concentration in this pool. Hence, particles can be formed in all these micelles. However, this does not occur, because the critical nucleus cannot contain less that two molecules. This contradiction is associated with incorrectness of using the notion of concentration for so small number of molecules. In this case, the processes of nucleation and intermicellar exchange should be considered in tandem. In practice, the following simpler approach was used: it was assumed that nucleation in one micelle required participation of a certain minimum number of P molecules. Due to the intermicellar exchange, this number of molecules was accumulated in some micelles and the nucleation occurred.

The micellar structure of solution can affects the synthesis of nanoparticles not only through the intermicellar exchange. For example, the model of Ostwald ripening in reverse microemulsions, which will be discussed below, considers micelles as complexes that contain reactants and move to the growing particles. In this case, the exchange proceeds between micelles and particles rather than between micelles.

On the whole, the modern models of synthesis of nanoparticles in reverse micelles fit the considered general scheme, which, as can be easily seen, allows for the existence of quite a lot of combinations of different chemical reactions and processes of nucleation and growth. Moreover, there are several types of schemes of synthesis in reverse micelles (blending of microemulsions, pouring of a solution into a microelusion, *etc.*), and a lot of models pertaining to one or another case have been described.‡

1. Models based on the LaMer diagram

The models described by the LaMer diagram consider the nucleation of particles under the conditions of gradual increase in the supersaturation and also their growth by adding the monomers. For these models to be applied, the coagulation should be neglected. This is possible, for example, if the mobility of particles is limited or if the surfactant adsorption on their surface prevents their coagulation. The aforementioned power law kinetics and the kinetics with cessation of growth are possible within the framework of such models. The power law kinetics is observed, for instance, when the particles grow under the conditions of approximately constant supersaturation. For the growth controlled by the diffusion of monomers, the particle size is proportional to the square root of time, whereas for the rate determined by a process of monomer addition, the particle size is a linear function of time. A version is possible where the particle size is determined by the rate of a chemical reaction that supplies the monomers. In this case, for the approximately constant reaction rate, the dependence of the particle volume on time is linear and the size is proportional to the cube root of time. After the end of this reaction, the kinetics with the cessation of growth is observed due to depletion of the reactants.

The first LaMer diagram-based model[8, 16, 32, 213] appeared in 1983. It was used for describing the synthesis of metal boride nanoparticles according to the procedure of pouring an aqueous solution of the reducing agent into a microemulsion. We assigned this process to those described by the LaMer diagram, because the aqueous solution was added gradually, drop by drop. According to this model, the precursor is randomly distributed in micelles. The number of nuclei is proportional to the number of micelles containing the precursor in the amount sufficient for nucleation

$$N_{\text{nucl}} = FN_{\text{M}} \sum_{k=i}^{\infty} p_k \,, \tag{8}$$

where N_{nucl} is the number of nuclei; F is the constant that takes into account the number of micelles reached by the reducing agent before the reactants have been redistributed due to intermicellar exchange; N_{M} is the number of micelles; i is the minimum number of ions required for nucleation;

$$p_k = \frac{\mathrm{e}^{-\lambda}\lambda^k}{k!}$$

is the Poisson distribution; λ is the average number of ions per micelle. The factor F takes into account the gradual introduction of the reducing agent to the system. However, we consider this way of taking account of this factor as insufficiently substantiated. According to this model, the average number of molecules (z) in the resulting particles can be found by the formula

$$z = \frac{\lambda}{F\sum_{k=i}^{\infty} p_k} \,. \tag{9}$$

It follows from this formula that for sufficiently large λ values, z should increase with the increase in λ. For small λ, the number of nuclei is small; hence, z should be high. It turns out that the concentration dependence of the particle size has a minimum. This conclusion was used in explaining experimental data. For a case where factor F is independent of concentration, it was shown that the critical nucleus contains two molecules.

Later, the model was extended to the case of mixing of two microemulsions.[69] The formula for the number of nuclei took the form

‡ However, due to the shortage of experimental studies directed at elucidation of mechanisms of nanoparticle nucleation and growth in reverse micelles, the use of these models under the specific conditions of synthesis was almost always controversial.

$$N_{\mathrm{nucl}} = FN_{\mathrm{M}}\left(\sum_{k=i}^{\infty} p_k\right)^2. \qquad (10)$$

In this formula, the squared sum is associated with the fact that for the nucleation of a particle in a single micelle, the latter should contain sufficient amounts of reactants from both microemulsions. The physical meaning of factor F was not explained in the discussed study.[69] The analysis of experimental results on the synthesis of AgBr nanoparticles with the use of this model showed that the aggregation number of the critical nucleus is 1.

The second model described by the LaMer diagram was discussed is a study [192] devoted to the synthesis of TiO_2 nanoparticles by mixing an AOT–water–isooctane microemulsion with a solution of titanium tetrabutoxide (TTB) in isooctane. Their mixing led to a slow hydrolysis of TTB

$$Ti(OBu^n)_4 + 4\,H_2O \longrightarrow Ti(OH)_4 + 4\,Bu^nOH,$$

followed by the condensation process

$$Ti(OH)_4 \longrightarrow TiO_2 + 2\,H_2O.$$

In this model, the loss of TTB is described by the following equation:

$$-\frac{dN_{\mathrm{TTB}}}{dt} = k_{\mathrm{h}}N_{\mathrm{TTB}}, \qquad (11)$$

where N_{TTB} is the number of TTB molecules; k_{h} is the unknown rate constant which can be found by analyzing the growth kinetics of nanoparticles. The intermolecular exchange in AOT-based microemulsions proceeded in the millisecond time interval, while the reactions of particle formation are slower; hence, the reaction rate depends on reactant distribution among the micelles rather than on the intermicellar exchange rate. This distribution is equilibrium, *i.e.*, the Poisson distribution

$$p_i = \frac{e^{-\lambda}\lambda^i}{i!},$$

where p_i is the probability that a micelle contains i molecules of the reactant, l is the average number of $Ti(OH)_4$ molecules per micelle,

$$\lambda = \frac{N_{\mathrm{h}}}{N_{\mathrm{m}}},$$

where N_{h} is the number of $Ti(OH)_4$ molecules, N_{m} is the number of micelles. The number of micelles containing precursors in amount (n) sufficient for nucleation is determined by the formula

$$N_{\mathrm{m},n} = N_{\mathrm{m}}\sum_{i=n}^{\infty} p_i. \qquad (12)$$

The nucleation rate is proportional to the number of micelles capable of nucleation

$$\frac{dN_{\mathrm{p}}}{dt} = k_{\mathrm{n}}N_{\mathrm{m},n}, \qquad (13)$$

where k_{n} is the unknown rate constant for nucleation. Assuming that the latter constant is independent of the particle size and proportional to the reactant concentration, the material balance equation can be written as follows:

$$-\frac{dN_{\mathrm{h}}}{dt} = n\frac{dN_{\mathrm{p}}}{dt} + \frac{k_{\mathrm{g}}N_{\mathrm{h}}N_{\mathrm{p}}}{N_{\mathrm{m}}} + \frac{dN_{\mathrm{TTB}}}{dt}, \qquad (14)$$

where k_{g} is the unknown constant characterizing the growth rate. These equations can be solved under the assumption of the absence of aggregation and Ostwald ripening. Within the framework of the model under consideration, it is possible to find the unknown constants (k_{h}, k_{n}, k_{g}) from experimental data; the aggregation number for the critical nucleus was found [192] to be five.

2. Coagulational models of growth

Within the framework of coagulation models, it is possible to consider the growth of particles as the result of only coagulation, whereas the growth due to the addition of monomers and the Ostwald ripening is ignored. This is possible if both the chemical reaction and the formation of particles are fast and the particle stability with respect to coagulation is insufficiently high. To eliminate the contribution of the Ostwald ripening to the overall growth kinetics, it is also necessary that the solubility of particles be sufficiently low.

The coagulation as the main growth mechanism for particles in reverse microemulsions was considered for the first time by Towey *et al.*[43] The coagulation process for nanoparticles in a reverse nicroemulsion is described by the following scheme:

$$M(P_n) + M(P_m) \rightleftharpoons M_2(P_n + P_m) \longrightarrow M(P_{n+m}) + M, \qquad (15)$$

where $M(P_n)$ and $M(P_m)$ are the reverse micelles containing P_n and P_m particles which consist of n and m molecules, respectively; M_2 is a dimer of reverse micelles. To describe the growth of CdS nanoparticles during their synthesis according to the method of blending of two micromulsions, it was proposed [43] to use the Smoluchowski model of rapid coagulation in which the rate constant of coagulation (k_{c})

$$P_n + P_m \longrightarrow P_{n+m} \qquad (16)$$

is replaced by the rate constant of intermicellar exchange (k_{ex})

$$M + M \longrightarrow M_2 \longrightarrow M + M. \qquad (17)$$

In Eqns (16) and (17), the concentrations of particles and reverse micelles were calculated per total microemulsion volume.

Robinson *et al.*[237] assumed, probably without sufficient substantiation, that after their nucleation, the CdS particles grew by the Ostwald ripening mechanism. The model proposed in Ref. 43 was used for analyzing the growth of silver nanoparticles. [61]

As was shown later [64] within the framework of the model proposed by Towey *et al.*[43] mentioned above, the kinetics of growth of CdS nanoparticles cannot be described in all time scales. According to this model, the rate constant for coagulation should be independent of the nature of nanoparticles and their size and be equal to the rate constant of

intermicellar exchange. However, the experimentally found k_c values for CdS and ZnS were different and decreased as the particles grew. Constant k_c was shown to be the exponential function of both the particle size and the parameter W. The dependence of the average particle size on the logarithm of time was roughly linear with the positive tangent. The model was refined by taking into account the fact that k_c decreased with the increase in the particle size. For $k_c > k_{ex}$, the particle size was controlled by the intermicellar exchange and the proposed model [43] was valid. When the particles grew so large that k_c became smaller than k_{ex}, the particle growth was controlled by coagulation. The particle distribution among the micelles became equilibrium and the coagulation rate was now proportional to the number of micelles containing two (and more) particles. The transition from one mode to another occurred upon the attainment of the particle size of 2.4 nm approximately in 0.02 s after microemulsions were mixed. The decrease in k_c with the increase in the size was assigned to the presence of a potential barrier to coagulation, which became higher as the particle size increased. Moreover, a study by McCartney and Levine [238] was cited in which the Derjaguin approximation for two spherical particles interacting due to the overlap of their electrical double layers was considered. However, neither estimates nor formulas were shown. The authors of another study [64] also suggested that the constant k_c depends on the ratio W and attributed this fact to the following two factors which operate with the attainment of a large particle size:

— the probability that two particles occupy the same micelles decreases,

— the particles are now coated by surfactant shells.

The k_c *vs.* W dependence was attributed to the fact that the particle growth was restricted by the micelle size. However, there were no grounds for this restriction, because the particle diameters were compared with the hydrodynamic diameters of micelles rather than with the diameters of their pools. If the particles are assumed to reside in water pools, then their diameters should be compared with the pool sizes rather than with the external sizes of micelles. Moreover, it is still unclear how the explanation based on the presence of an activation barrier arising due to the overlap of electrical double layers agrees with another explanation assuming that the particle growth is limited by the micelle size. Analogous kinetic relationships for the growth of particles were observed for PbS,[71] mixed CdS/ZnS particles [70] (these particles were also synthesized in an earlier study [66] but its authors did not describe the mechanism), AgBr and AgI.[79] For AgI nanoparticles with diameters < 4.5 nm, rapid coagulation (controlled by intermicellar exchange and described by a simple model) was observed;[43] for AgBr and PbS nanoparticles, the coagulation was slow.

Later, the discussed [64] model was developed further [98] and applied to the synthesis of CdS nanoparticles. The expression for the rate constant for coagulation was derived within the framework of the Derjaguin model of the dependence of the interaction energy of spherical particles on their diameters under the approximation of short-range forces

$$k_c = C_1 \exp\left(-C_2 \frac{2d_1 d_2}{d_1 + d_2}\right), \tag{18}$$

where C_1 and C_2 are the unknown constants, d_1 and d_2 are the diameters of colliding particles. Modelling led to sufficiently narrow distributions ($\sim 10\%$), which in this particular case were consistent with the experimental data for $W = 3$ and 6 but deviated from experimental data for $W = 10$. Unfortunately, the authors of the latter study [98] did not cite the earlier paper [78] dealing with quite similar matters in which the growth of CdS nanoparticles during the synthesis in AOT-based reverse micelles was experimentally investigated. In the latter study,[78] a model was proposed according to which the particles had a certain size distribution and a notion of the threshold particle diameter in the distribution (d_{th}) was introduced defined as the intercept of the size axis by a tangent to the descending branch of the distribution curve in the inflection point. In essence, d_{th} is the size of the coarsest particles in the distribution. The d_{th} value was found from the absorption spectra under the assumption that this value correlates with the position of the long wavelength absorption edge (l_{th}), which was determined in a similar way. The dependence of d_{th} on the time logarithm had several inflections, whereas in the former study,[98] this dependence was close to linear. This can be explained by the fact that in the latter study,[78] the particle growth was examined in the much wider time interval. For the size range studied in the former study, [98] the growth kinetics was the same in these two papers.

According to the model under consideration,[78] the particle growth proceeded due to coagulation. The coagulation rate was controlled by the fusion of micelles containing CdS particles. The existence of two critical particle sizes, namely, d_c and $2^{1/3}d_c$, the attainment of which marked substantial deceleration of the growth, was postulated

$$k(n,m) = \begin{cases} k_0, & \max(n,m) < n_c, \\ k_1, & n_c < \max(n,m) < 2n_c, \\ k_2, & \max(n,m) > 2n_c, \end{cases} \tag{19}$$

where $k_0 \gg k_1 \gg k_2$; n and m are the aggregation numbers of colliding particles; n_c is the aggregation number corresponding to d_c; k_0 is the rate constant for the intermicellar exchange. The presence of two plateaus in the curve of the increase of d_{th} with logarithm of time was explained by the proposed model. According to the results of simulations, in the initially wide distribution, as the aggregation number approached n_c, a peak appeared in the vicinity of n_c; insofar as the particles could not grow further ($k_0 \gg k_1$), this peak extended to $2n_c$. Then, the redistribution into the interval from $2n_c$ to $4n_c$ took place. Thus, this model differs from that discussed above [98] by the different form of the dependence of the coagulation constant on the particle size.

The dependence of the particle size on the logarithm of time for the coagulational mechanism of growth can be obtained as follows. For colliding particles with equal radii, the activation energy (E_a) of the coagulation process is a linear function of the radius (R)

$$E_a = CR, \tag{20}$$

where C is a constant. The growth rate of particles with this activation energy can be approximated as [239]

$$\frac{dR}{dt} = V_0 \exp\left(-\frac{CR}{kT}\right), \tag{21}$$

where V_0 is the growth rate for the zero barrier. Integration of Eqn (21) affords

$$R = \frac{kT}{C}\ln\left[\frac{CV_0}{kT}t + \exp\left(\frac{CR_0}{kT}\right)\right], \quad (22)$$

where R_0 is the initial particle radius.

Thus, for the coagulational mechanism of growth, it is evident that the time dependence of the particle size has the logarithmic form.

3. Model of Ostwald ripening

If both the chemical reaction and the nucleation of particles stopped and the coagulation can be neglected, then the only way left for the particle growth is the Ostwald ripening. The Ostwald ripening in reverse micelles was actively studied.[210–212, 219] To find the real mechanism of nanoparticle formation in reverse microemulsions, the highly reliable double-jet method was used for synthesizing AgCl nanoparticles in both reverse micelles and a common aqueous gelatine solution. In the two-jet method, both reactants (KCl and $AgNO_3$) were fed into the reactor at a constant rate. As shown in publications[210–212] the synthesis in reverse microemulsions does not in principle differ from the synthesis in the gelatine solution and can be reduced to the Ostwald ripening. The differences are only quantitative, namely, due to the very poor solubility of gelatine in this system, the ripening is slower. Micelles containing the reactants are considered as the complexes that travelled to the growing particles due to diffusion. The fact that the diffusion coefficient of micelles is lower than that of molecules also favours the smaller size of synthesized particles.

Nanoparticles of AgCl were also synthesized[210] by the instantaneous mixing of the microemulsion with the reactants. The experimental results were successfully described as the common Ostwald ripening. Moreover, no limitations on the particle size by the micellar pool size were observed.

A criterion that allowed the growth due to coagulation to be distinguished from the growth due to the Ostwald ripening is proposed in studies[211, 219] devoted to the synthesis of monodispersed particles. For the growth rate independent of the particle concentration, the coagulation takes place; in the opposite case, the Ostwald ripening is observed. Based on this criterion, it was concluded that the AgCl growth in a NP-6-based microemulsion proceeded by the ripening mechanism, whereas its growth in the AOT-based microemulsion followed the coagulational mechanism. This criterion was used[64, 79] to analyze the experimental data discussed above. Based on this analysis, it was concluded that the growth of ZnS, AgBr and AgI nanoparticles occurred by the Ostwald ripening, whereas CdS particles grew due to coagulation. However, from our point of view, taking into account the accuracy of the data from the cited publications, the use of the proposed criterion does not allow one to conclude unambiguously on the growth mechanism.

A theory that provides the general description of the syntheses carried out in both aqueous solutions and micelles was proposed.[219] This theory is based on the following three assumptions:

— the delivered reactants are consumed for the nucleation and the growth of particles,

— the reactants delivery rate is independent of the subsequent precipitation,

— for the fixed rate of reactant delivery, the nucleation rate is controlled by only the growth of nuclei.

The conclusion drawn based on these assumptions is as follows: the number of particles formed is directly proportional to the reactant delivery rate and inversely proportional to the particle growth rate. In essence, this theory can be considered as a model based on the LaMer diagram.

V. Computer simulations

The theoretical models discussed above reflect quite adequately the general features of the processes of nucleation and growth of nanoparticles in supersaturated solutions, but virtually ignore the specificity of these processes in reverse microemulsions, first of all, the intermicellar exchange. Apparently, this is associated with the difficulty of their analytical description. The use of methods of computer-assisted simulation makes it possible to model the intermicellar exchange on the detailed level virtually without any complications. This involves setting the rules for the exchange of reactants upon the collision of micelles and taking into account the spatial distribution of micelles.

Let us consider the approaches to modelling of a typical synthesis in which the particles are formed from the product of reaction (6). The latter proceeded upon the blending of two microemulsions with reactants A and B in their aqueous pseudophases. First of all, the following two sets of reverse micelles were created: micelles of the first set contained reactant A and micelles of the second set contained reactant B. The number of reactant molecules in a micelle was usually assumed to be a random discrete value distributed according to the Poisson law (in some studies, this value was assumed to be continuous).[240] Then, two sets of micelles were mixed thus imitating the blending of two microemulsions. Mixing of micelles triggered the intermicellar exchange. The latter was usually modelled by the multiple repetition of the elementary step of exchange, which consisted of the random selection of two micelles and the use of them in a certain speculative scheme of intermicellar exchange. This approach corresponds to the typical real situation where the intermicellar exchange rate is not controlled by the micelle diffusion. However, in some studies, more comprehensive modelling of the intermicellar exchange was carried out by taking into account the diffusion of micelles in the space. For this purpose, the random walk of micelles over the spatial two-dimensional[215, 216, 241, 242] or three-dimensional[217, 243] nets was considered. In should be noted that for the reaction so slow that uncontrolled by the intermicellar exchange, it is unreasonable to take account of the latter factor and the consideration may be restricted, for instance, to solving a system of common differential equations such as Eqns (11)–(14). This simulation procedure was accomplished[203] for the synthesis of palladium nanoparticles by the reduction of $PdCl_2$ under the action of sodium hypophosphite.

Next, the rules that determine the processes in the elementary step of intermicellar exchange were established. For a collision of two micelles of which one contained A molecules and the other contained B molecules, it was usually assumed that their contents are mixed, reaction (6) proceeds immediately according to its stoichiometry and the excessive reactant is redistributed in a certain fashion

between these micelles. For the number of product molecules P larger than in the critical nucleus, the particles were usually assumed to form instantaneously; however, sometimes, the classical nucleation theory was used to assess the probability of their formation.[244, 245] If the number of molecules P was smaller than in the critical nucleus, then these molecules were redistributed in a certain fashion between the colliding micelles. Several modes of such redistribution were considered,[246] namely, the cooperative (after the collision, the whole amount of substance passes to one micelle, Fig. 5 *a*), binomial (the substance is equally distributed between micelles, Fig. 5 *b*) and random. The cooperative exchange mode corresponds to the attractive interaction between P molecules, the binomial mode corresponds to their repulsive interaction and the random mode corresponds to the absence of interaction.

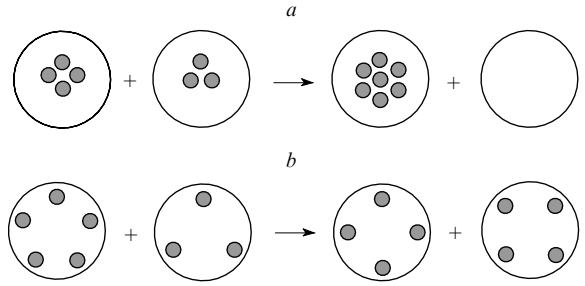


Figure 5. Versions of intermicellar exchange determined by whether the interaction between molecules is attractive or repulsive. Exchange: (*a*) cooperative, (*b*) binomial.

If a micelle involved in the elementary step of intermicellar exchange contains a particle and product P is also present, then the whole amount of product was assumed to be immediately consumed in the particle growth. If the elementary step of intermicellar exchange involves two particles, then it is usually assumed that the latter do not coagulate but grow consuming the available product. In the process, the product can be consumed totally in the growth of one of particles or in the growth of both particles in proportion to their surface areas.[240] In order to improve the agreement between the calculations and experimental results, in certain studies the possibility of coagulation of particles was also considered. Different mechanisms of limiting the coagulation were discussed. For instance, it was assumed that the coagulation is impossible if the size of the resulting particle exceeds the micelle size;[139, 141, 218, 247] that the exchange occurs *via* a certain channel between the colliding micelles and coarse particles cannot pass through this channel;[241] and that the coagulation decelerates with the increase in the particle size.[248]

For the results of simulations to be statistically reliable, it is necessary to use sufficiently large numbers of micelles, which dramatically increases the computation time. This is why the modelling algorithm requires optimization, which consists, for example, in eliminating the inefficient collisions of empty micelles.[249]

Analogous approaches were also used in modelling the synthesis of nanoparticles by mixing microemulsions with aqueous[250] or oil solutions containing one of reactants, or by the bubbling the reactant through the microemulsion.[251, 252]

VI. Conclusion

The method of synthesis of nanoparticles in reverse microemulsions appeared $\sim$30 years ago. Since that time, this method was used in the synthesis of different inorganic substances; moreover, in the half of cases, the polydispersity not higher than 20% was achieved. The main drawback of this method is the small concentration of synthesized nanoparticles. Moreover, there is no universal theory suitable for designing this synthesis. Apparently, this is associated with the presence of a lot of hypotheses which, despite being insufficiently substantiated, were used in explaining the results of syntheses. For example, the idea that the reverse micelle shells can spatially limit the particle growth proved to be incorrect.

The main features of the synthesis of nanoparticles in reverse microemulsions can be explained as follows. The small size of synthesized particles and their stability with respect to coagulation are associated with the high surfactant concentration calculated for the pseudophase in which the reaction occurs. The narrower size distribution as compared with conventional methods is associated with the better mixing of reactants, because the rate of formation and growth of particles in reverse microemulsions is lower as compared with aqueous solutions. The nonsphericity of synthesized particles can also be easily explained by the effect of adsorption on the growth rate of different crystal faces.

The theory of synthesis of nanoparticles in reverse micelles should for the largest part consist of such general assumptions and be supplemented by a small specific part dealing with the intermicellar exchange. In the available studies on the simulation of particle growth, attention was focused on this specific part, whereas the general problems such as the nucleation and the growth are still insufficiently clear. The intermicellar exchange can be easily simulated, but the major problem is what equations should be used for describing the rates of nucleation and growth. Usually, the classical nucleation theory was used together with the assumption of the instantaneous growth within a micelle. However, this theory is very inaccurate and the mechanisms of crystal growth are diverse.

For a part, the development of the theory was hindered by the absence of reliable experimental data on the kinetics of particle growth depending on different parameters of the synthesis. This is explained by the fact that the majority of studies were aimed at the development of methods for synthesizing nanoparticles with definite properties rather than at studying the mechanisms of their growth.

Thus, although the method of synthesis in reverse microemulsions is insufficiently substantiated, it can be used in cases where the particles need not have too narrow size distributions or too high concentrations.

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