Ultrafine Metal Particle Formation in Reverse Micellar Systems: Effects of Intermicellar Exchange on the Formation of Particles

Upendra Natarajan,† Kalyan Handique, Anurag Mehra, Jayesh R. Bellare, and Kartic C. Khilar* Department of Chemical Engineering, Indian Institute of Technology, Bombay 400 076, India

Received July 25, 1994. In Final Form: February 26, 1996

A modeling approach is developed to account for the important effects of intermicellar exchange on the ultrafine particle formation in reverse micelles. A set of fusion–fission schemes is specifically proposed and used for modeling intermicellar metal exchange. The dynamic effects largely differing in their time scales are decoupled using a two-staged approach. Growth of metal particles is simulated to occur through intramicellar attachment of free metal atoms from an instantaneous reduction reaction and as well as by transfer and attachment through intermicellar exchange. Simulation results predict increase in particle size with aqueous core size and total aqueous phase volume, increase in particle number density with surfactant concentration at fixed aqueous phase to surfactant molar ratio, a minimum in average particle size as a function of salt concentration, and increase in particle size polydispersity with salt concentration and aqueous core size. Low values of the order of 10–1 are found for the number ratio of particles to micelles. All these effects have been observed experimentally. The mean core size and the critical metal nucleation number are found to be the primary influencing parameters for the final particle sizes. It is further found that the polydispersity can be controlled through proper choice of starting mixture conditions.

1. Introduction

Ultrafine metal particles are finding new applications as catalysts, magnetic materials, and overbased additives in lubricants. Quantum size effects have been observed for particles of nanometer dimensions. Their small size and the material properties at these sizes offer novel application possibilities. Reverse micellar systems are currently being explored for making ultrafine particles of a variety of metal and alloy species. The principal reason for using reverse micelles is the extremely small size of the aqueous micellar cores in most organic apolar solvents. The use of surfactant aggregates for controlled particle synthesis is an emerging technology to which importance has been given only in the past few years. It forms a powerful method for controlling particle sizes and their size distributions. The books by Fendler2,3 provide good treatises on reverse micellar systems.

Reverse micelles offer some advantages not realized through processes based on conventional methods using homogeneous reaction media. Control of particle size and its distribution and enhancement of reaction rates are the two known major advantages of the micellar route. The review article by Pileni4 is a recent informative source on the experimental investigations pertaining to the formation of ultrafine particles using reverse micelles as microreactors. A number of experimental investigative efforts in producing metal colloidal particles have been undertaken over the years.5–21 Boutonnet et al.5 and Gobe et al.6 were one of the earliest to study metal particle formation in these systems. Kurihara et al.7 showed that, under identical conditions, a great number of particles are formed in water-in-oil (w/o) microemulsions than in homogeneous solutions and that the particles formed are smaller and more uniform in size. Khan-Lodhi8 has experimentally studied the formation of platinum, palladium, and gold particles. The work of Nagy et al.9 for preparation of Ni–B and Co–B and Ni–Co–B alloy, by reduction using NaBH4 in the water/CTAB/hexanol system shows the effect of salt concentration and discusses the possible role of a critical metal particle nucleation number and the effect of intermicellar exchange in regulating particle growth. Significant research has also been performed on the formation of carbonate particles.10,13 Iron,14,15 CdS,17 PbS,21 and CdS and ZnS composites22 are some of the other types of metal particles synthesized in these systems. Formation of YBa2Cu3O7–x particles has also been reported using w/o microemulsion with a

(15) Lopez-Quintela, M. A.; Rivas, J. J. Colloid Interface Sci. 1993, 158, 446.
micelles has been achieved. In a recent study, preparation of large nanosize CdS particles by using functionalized surfactants would require the use of population balances. The work presented here aims at developing an approach to incorporate the important effects of intermicellar exchange on the formation of particles in a monodisperse reverse micellar system. It is concerned with an instantaneous reaction in the aqueous core, and hence the kinetics of the intramicellar reaction is not considered. Furthermore the surfactant–micelle exchange process is neglected. Though the model developed here is applied to formation of ultrafine metal particles in reverse micelles, its approach and framework for describing intermicellar exchange process are however reasonably general enough and may be applicable to other similar systems. In the following section, a stochastic model is discussed for describing intermicellar exchange through the fusion–fission mechanism. Extensive model calculations have indeed existed. Partial opening of the surfactant layer or interfacial transfer of aqueous pool solubilizes present close to the micelle surface can result in the partial exchange of material.

Under equilibrium conditions, the size and the aggregation number of the reverse micelles are dictated by thermodynamics and equilbrium transport between micellar and bulk phases. As evident from experimental reports, even the molecules of different coexisting species follow distributions of their occupancy numbers, which is defined as the number of a particular species solubilized in the micelle core. For noninteracting and random kinetics, the distribution is known to be Poissonian. Geometric and binomial distributions can result under other conditions.27 This feature clearly leads to a situation different from continuum conditions. The typical time scales that have been reported for different mechanistic effects in polar micellar systems are28,29 1–10 ns for diffusion controlled intramicellar reaction, 50–100 ns for the lifetime of a pair of reactants confined to the micelle core, 300–500 ns for the formation of an encounter complex via diffusion on the micellar surface, 1–100 ns for a diffusion-controlled entry of a surfactant molecule onto the micellar surface from the bulk phase, 0.1–1 µs for diffusion-controlled collision of micellar aggregates, and 0.1–1 ms for intermicellar exchange to occur.

Though reverse micelles have been studied in detail and are well characterized using the AOT systems, the mechanistic details of reactions of finite rates, ultrafine particle formation, and growth seem to have not been studied through a single consistent mathematical model. Recently Bommarius et al.29 and Hatton et al.30 have presented a model based on population balances to clearly account for the effect of an instantaneous, irreversible reaction. They have also considered the effects of some known initial equilibrium distributions and redistribution interaction potentials, on the temporal evolution as well as the steady state solutions of the solute dispersions. The stochastic framework has been very recently applied to monodisperse system reaction kinetics with exchange, by Barzykin and Tachiya.31 Fusion–fission of micelles was considered in their work in a restricted way with a formalism based on single-particle-hopping during collisions in a monodispersed micelle size system.

The work presented here aims at developing an approach to incorporate the important effects of intermicellar exchange on the formation of particles in a monodisperse reverse micellar system. It is concerned with an instantaneous reaction in the aqueous core, and hence the kinetics of the intramicellar reaction is not considered. Furthermore the surfactant–micelle exchange process is neglected. Though the model developed here is applied to formation of ultrafine metal particles in reverse micelles, its approach and framework for describing intermicellar exchange process are however reasonably general enough and may be applicable to other similar systems. In the following section, a stochastic model is discussed for describing intermicellar exchange through the fusion–fission mechanism. Extensive model calculations have

---

**Figure 1.** Schematic representation of entities and some dynamic physicochemical effects in a reverse micellar system. The reverse micellar system is extremely dynamic in nature. Some of the interactive effects, believed to occur in this system, are shown through mechanistic schemes in Figure 1. They include the exchange of surfactant molecules, solutes in the aqueous phase, species which may be preferentially distributed in one of the phases, and the solid particles formed on reaction followed by nucleation. As shown in Figure 1, some of the basic system interactions include the exchange of surfactant molecules between reverse micelles and bulk phase (SE), the formation—breakup of dimers, trimers and lower level aggregates which may be present in relatively small concentrations, intermicellar fusion—fission of reverse micelles (RMFF), and effects involving solute species such as intramicellar kinetic reactions (metal salt reduction SR), metal particle nucleation (PN), and growth via intramicellar attachment and intermicellar exchange of aqueous phase contents. The intermicellar exchange of contents leads to a distribution of material throughout the system, and a mathematical description of this phenomenon would require the use of population balances. Eicke et al.30 were the first to show that an intermicellar material exchange through a fusion–fission mechanism

---

been conducted for a wide range of system/operating conditions. The model predictions of the size and the number of metal particles formed are found to be in reasonable agreement with measurements reported in literature. Some new insights have also been obtained from this simulation of ultrafine particle formation.

2. A Stochastic Model

2.1. Assumptions and Model Considerations. Attention is drawn to Figures 1 and 2 for reference.
1. The reducing agent is introduced into the continuous phase. Its diffusion into the reverse micelles proceeds faster than the intermicellar exchange process.
2. The only entities of consequence and present in significant amounts are stable reverse micelles of a constant aggregation number. The aggregation number is determined by micellar thermodynamics.
3. Metal particle nucleation and intermicellar exchange of aqueous droplet contents are the only effects that have been considered.
4. An instantaneous reaction is assumed. In the present model, however, the influence of reaction kinetics is not important since the intermicellar exchange is slow and governs the growth of particles.
5. The initial distribution of salt molecules is taken to be Poissonian and it also gives the initial distribution of metal atoms in the present case.
6. Binary fusion–fission process is taken to be the mode of intermicellar exchange where the kinetics is governed by a constant pseudo-first-order frequency $\alpha$ where $\alpha = k_w M_{\text{tot}}$ and $k_w$ is the second-order exchange rate coefficient. The rate-limiting step is assumed to the fusion of two reverse micelles, while fission of the unstable transient dimer is assumed instantaneous in relation to the time scales of the other steps in the overall process.
7. Nucleation is assumed to occur when the number of metal atoms inside the reverse micelle reaches a critical nucleation number, $n^*$. 

2.2. Mathematical Formulation. The stochastic approach for small systems provides a well-defined method for the analysis of statistical fluctuations. This approach has been applied to small systems with simple kinetic schemes, which lead to analytical solutions as presented by McQuarrie et al.29 This method, along with a population balance formulation into the stochastic master equation, provides a framework that is appropriate for dealing with reaction kinetics as well as dynamic movement of materials along the micelle microreactors during intermicellar exchange. The reaction rate in each micelle depends on the number of reactants it contains, while only the global effect summed up over all micelles is experimentally observed. It has been shown experimentally by Bommarius et al.29 and theoretically by Hatton et al.,30 that a second-order continuum model for intermicellar exchange leads to significant errors. A stochastic equation, for a simple intermicellar reaction in normal micelles, has been given by Rothenberger and Infelta28 and used for solving the equilibrium initial reactant distributions.

For the purpose of studying the effects of the intermicellar exchange process and based on the typical time scales for salt reduction in reverse micellar systems presented earlier in this section, we propose a two-stage approach to treat the particle formation process. In stage I, the salt molecules in the reverse micelles get reduced to metal atoms without being affected by the intermicellar exchange process, while in stage II, intermicellar exchange takes place between reverse micelles containing only metal atoms or nucleated metal particles. The present work considers instantaneous salt reduction kinetics, which has been affected by means of two very rapid processes of nanosecond time scale: diffusion of reducing agent from the continuous phase into the reverse micelles and the reaction inside the reverse micelle. The model in the present work follows a discrete stage continuous time process,33 possessing Markov chain property.34 The intermicellar exchange is formulated to simulate a continuous parameter Markov process. It may be noted that the two-stage approach will be really useful when the salt reduction reaction is not instantaneous but proceeds faster than the intermicellar exchange. This case is however not treated here.

2.2.1. Stage I. The intramicellar reaction $A \rightarrow M$ is considered (Scheme I in Figure 2), where $A$ is the metal salt and $M$ is the free metal atom. An instantaneous reaction between the salt and the reducing agent is used. Metal particle formation and growth in this stage occur via the following mechanism

$$zA \rightarrow zM \rightarrow (P)_z \text{ (nucleation)}$$

Particle growth proceeds very fast on the basis of the assumption that the resistance to the attachment of free metal atoms onto the growing particle is negligible. We next present an initial distribution of salt molecules in reverse micelles. In the present case of rapid diffusion of reducing agent and an instantaneous intramicellar reaction, this distribution is also the initial distribution of metal atoms which then changes due to intermicellar exchange.

---


A. Initial Distribution of Salt Molecules. The Poissonian distribution is chosen for distributing the salt molecules in the reverse micelles at \( t = 0 \). As mentioned aptly by Almgren, this distribution is a normal starting point in distributing reactants in low numbers in micelles. This is also supported by most experimental observations using fluorescence quenching techniques and excimer formations and triplet energy transfer. A strong deviation from the Poissonian distribution is observed in cases where the mean salt occupancy number \( \mu_x \) is needed. Using a value of \( \mu_x \), the probability \( p_x \) is set according to

\[
p_x = \frac{(ux)^x e^{-ux}}{x!}
\]

starting with \( x = 0 \) and continuing until \( p_x \) becomes numerically negligible and less than a tolerance value which can be independently set. The largest value of \( x \) for which \( p_x \) is greater than this tolerance, defines the \( x_{\text{max}} \). The values of the mean number of salt molecules \( \mu_x \), the total reverse micelle concentration \( M_{\text{tot}} \), and \( V_{\text{mic}} \), the volume of the reverse micelle aqueous core are calculated using the expressions

\[
\mu_x = \frac{C_{\text{sa}} V_{\text{at}} N_{\text{agg}}}{(S - \text{CRMC}) V_{\text{org}}}
\]

\[
M_{\text{tot}} = \frac{(S - \text{CRMC}) A}{N_{\text{agg}}}
\]

\[
V_{\text{mic}} = \frac{V_{\text{at}} N_{\text{agg}}}{(S - \text{CRMC}) A V_{\text{org}}}
\]

where a critical reverse micelle concentration (CRMC) analogous to the critical micelle concentration for normal micelles is used.

B. Distribution at the End of Stage I. Stage I ends when all salt molecules, within every micelle, react to give metal atoms. For the given mode of introduction of the reducing agent and for the reaction \( A \rightarrow M \), the initial salt distribution is exactly translated into the final metal atom occupancy number distribution, and vice versa, which is \( p_x = 1 \) for \( x = 0 \) and \( p_x = 0 \) for \( 0 < x < x_{\text{max}} \). It may be noted here that if the reducing agent is introduced in the form of a microemulsion, then calculations in stage I are necessary.

2.2.2. Stage II. In this stage we consider the intermicellar exchange by a fusion–fission type of mechanism. It has been shown that for well-defined droplet dispersions, such as those formed by AOT, the exchange rate coefficients, \( k_{\text{ex}} \), are about a factor of \( 10^3-10^4 \) lower than the diffusion-controlled reaction rate of the order of \( 10^6 \) mol\(^{-1}\)L\(^{-1}\)s\(^{-1}\). In order to quantify the effects of this exchange on the metal particle formation, we propose the following fusion–fission rules.

A. Fusion–Fission Rules. These rules, which are shown through Scheme I in Figure 2 in the form of kinetic equations, are as follows:

1. Fusion of micelles each contributing free metal atoms will result in a metal particle inside the dimer if the combined number of free metal atoms equals or exceeds \( n^* \).
2. For the combined number of free metal atoms being less than \( n^* \), the result will be an accumulation of the free metal atoms into one of the micelles after the completion of the fission. Thus we have used a cooperative redistribution law for the rule describing the effect that decolalisation would have on the metal atom occupancy characteristics. In both 1 and 2, as a result of fusion–fission, an empty micelle is necessarily formed.
3. Fusion of micelles, of which one contains a metal particle and the other has free metal atoms, will give a micelle with a larger particle due to attachment of free metal atoms to the particle and will also result in an empty micelle. The cooperative law in Scheme 2 and 3 leads to bimodal distributions as there is a large fraction of empty micelles that are generated.
4. When micelles, each containing a metal particle, undergo fusion–fission, the particles do not agglomerate (secondary growth process) and are retained in their respective micelles.

B. Stochastic Equations for Fusion–Fission. The complete set of equations for this stage is given in Appendix I. If \( p_z \) denotes the occupancy probability of metal atoms (in the free state if \( z < n^* \) or particle form if \( z \geq n^* \)), then the set of equations

\[
dp_z/dt = R_1 - R_2
\]

\[
R_1 = k_a (\sum_{z=2}^{z-1} p_z p_{z-2} - \sum_{z=n^*}^{z=n^*} p_z p_{z-2}) \text { for } 2n^* \leq z \leq z_{\text{max}}
\]

\[
R_2 = -\alpha p_z (\sum_{z=2}^{z-1} p_z - \sum_{z=n^*}^{z=n^*} p_z) \text { for } n^* \leq z \leq z_{\text{max}}
\]

describes the temporal evolution of \( p_z \). Here \( k_a = \alpha/2 \) if \( z = z^* \) and \( \alpha \) if \( z = z^* \). \( R_1 \) is the rate of generation of \( z \) by the fusion of state \( z - 2 \) with the state \( z \), with \( z \) being less than \( z^* \). The rate of loss of state \( z \), given by the term \( R_2 \), is due to fusion of \( z \) with any other state \( z^* \) taking into account only the effective fusion steps in the overall scheme. The set of fusion equations is written according to the fusion rules and kinetic schemes in Figure 2. Since fission of the transient micelle does not lead to fission-based redistribution of free metal atoms or metal particle, according to the fusion–fission schemes, the need for including fission terms in the population balance for state \( z \) is thus obviated. Under such conditions, the expectation values encountered in the population balance approach do not figure in the equations. The fusion rate coefficient, \( \alpha \), is treated here as a lumped parameter representing the dynamics of the fusion process from beginning to end: collision of reverse micelles, opening up of surfactant cage, formation of dimer, mixing of contents, and attachment of free metal atoms onto metal particle. The fission of the transient dimer along with transfer of metal particle into one of the reverse micelles is assumed instantaneous. The set of fusion equations is integrated starting with the final distribution of \( p_z \), from stage I. The domain \( \Omega_z \) expands during fusion–fission and therefore has to be updated continuously to satisfy material balance and eliminate finite domain errors. The integration scheme
is as follows. The initial significant domain is obtained from stage I. The initial "expansion zone" domain \( \Omega = \{ z_{\text{max}} < z \leq 2 z_{\text{max}} \} \) is set along with the "significant domain". The equations for \( \Omega = \Omega_1 + \Omega_2 \) are integrated until the end of a time step, at which point an expansion step is made. The timestep size is greater than the actual integration step taken to meet accuracy conditions. The expansion check essentially checks whether any \( p_z \) values in \( \Omega_2 \) become greater than a minimum specified tolerance value set as an indicator of significant population. The newly induced states with significant values, along with their stochastic equations, are included into \( \Omega_2 \) and a new \( \Omega_2 \) is again specified. The integration is carried on until the end of this stage. The end of stage II occurs when all free metal atoms have been taken away by growing metal particles. Numerical completion is achieved when the relative change in \( p_z \) for all \( z \in \Omega_2 \) is less than an error tolerance value. This also amounts to negligible expansion of the domain.

2.2.3. Particle Size. The metal particle size is calculated assuming spherical particles and packing fraction for a specified lattice. The equations

\[
\begin{align*}
V_p &= \frac{1}{\Phi} 2V_{\text{met}} \\
\rho_p &= \frac{3}{4\pi} \left( \frac{3}{4\pi} \right)^{1/3} \rho_p
\end{align*}
\]

are used where the packing fraction \( \Phi \) for a face centered cubic lattice has been taken for the metal particle.

2.2.4. Simulation Details. The nonlinear coupled differential equations were integrated using Harwell subroutine DCO3AD based on Gear's backward differentiation formula implicit method. A comprehensive computer program makes use of this subroutine. The numerical parameters employed in the simulation are discussed in the next section.

**A. Initial Distribution Truncation.** The Poissonian distribution for the initial salt distribution in stage I is truncated when \( p_z \) becomes less than \( 10^{-5} \) during the calculation of \( p_z \) for various \( x \). The \( x_{\text{max}} \) value which sets this cutoff depends on \( \mu_x \) and increases as the parameter increases.

**B. Stochastic Domain Expansion Factor and Significance Value of Newly Formed States.** At any given time the actual set of stochastic equations is solved for \( z \) in the domain \( \Omega = \Omega_1 + \Omega_2 \) which includes the expansion zone. The factor of expansion for the simulation was kept at 2, which means that at any time the metal particles of higher concentration number, resulting only from a single binary fusion of metal atom number sets, are tracked simultaneously. New significant states are deemed to have formed if their \( p_z \) values are greater than \( 10^{-5} \).

**C. Completion of Stage II Numerical Simulation.** The simulation is taken to be complete when the relative change in \( p_z \) between successive time steps is less than \( 10^{-5} \) for all \( z \) in \( \Omega_2 \). This gives a sufficiently small error of \( 10^{-7} \) in \( \rho_p \). The \( z \) state domain does not expand on completion of the fusion–fission process.

3. Results and Discussions

First, results from a base case of mixture conditions are portrayed to show basic model features. This is followed by the effects of salt concentration, surfactant concentration, water to surfactant molar ratio, and the mean aqueous core volume, on the metal particle size distribution. Furthermore, the effect of the critical nucleation number on the particle size distribution is investigated through a parametric sensitivity analysis. The range of physical parameters in reverse micellar systems used in the simulation as well as the physical parameters used in a base case are presented in Tables 1 and 2, respectively.

### 3.1. Base Case Simulation Results

The water–AOT–cyclohexane system with the formation and growth of Ni-B particles is simulated. The base set of conditions is as follows: salt concentration, \( C_{\text{salt}} = 0.1875 \) M; surfactant concentration, \( S = 0.1 \) M; total water volume, \( V_{\text{aq}} = 2.5 \times 10^{-6} \) m³; the total cyclohexane volume, \( V_{\text{org}} = 166.3 \times 10^{-6} \) m³. Using the values of the physical properties from Table 2 and using eqs 2–4, the values of \( R, \mu_x, M_{\text{tot}}, \) and \( \nu \) are 3.35, 1.594, and 1.065 × 10^12 m⁻³ and 1.421 × 10⁻²⁶ m⁻³ (corresponding to a 1.5 nm core radius), respectively.

Figure 3 shows the metal atom occupancy number distribution. The curves are shown at the end of stages I and II. The distribution at the end of stage I replicates...
the initial distribution of salt molecules and peaks at \( \mu_s = 1 \), corresponding to the low values of 1.594 for \( \mu_s \). A large percentage of micelles containing either free metal atoms or no metal atoms, of about 70%, are present since for this particular set of conditions \( \mu_s \) is much smaller than \( n^* \). This clearly shows the transformation from a unimodal random Poisson distribution for \( x \) at equilibrium, to a bimodal distribution at the end of stage II, arising from cooperative free metal–free metal and free metal–particle cooperative interactions according to the fusion laws used here.

The maximum occupancy number of metal atoms at the end of stage I, with significant population probability, is about 10 in the reverse micelle. The metal atom distribution after fusion–fission shows a high fraction of empty micelles (about 88%). This is a manifestation of the fusion schemes according to which every fusion leading to an effective change in the metal atom distribution will also result in the generation of an empty micelle. In general, the greater the number of reverse micelles containing free metal atoms, the greater would be the final number of empty micelles and therefore smaller the number fraction of micelles containing particles. The population of micelles having particles constituted by greater than six metal atoms increases by a significant amount during the intermicellar exchange process.

Another result is the generation of nuclei during intermicellar exchange. The number of new nuclei formed for the base case is about 20% of the total micelle population. The mean particle diameter at the end of stage II is 1.45 nm, corresponding to a mean metal Ni\(_2\)B occupancy number of 6.7. The average particle occupancy number has increased from 4.4 to 6.7 during stage II. This is translated into an increase in mean particle size from 1.26 to 1.45 nm. The final occupancy number and size distribution depend only on the absolute and relative values of \( \mu_s \) and \( n^* \). The value of \( n^* \) in relation to the value of \( \mu_s \) can control the relative effect of salt reduction and intermicellar exchange. The results in Figure 3 also show some polydispersity in the final particle sizes, due to the large fraction of free metal atoms available after the reduction reaction, leading to a significant population of high metal occupancy micelles.

3.2. Parametric Studies. The following parameters were kept constant to show the effect of mixture conditions: intermicellar exchange rate constants \( \alpha, \text{CMC, and } \nu_k \). These parametric values are shown in Table 2. The effects of \( R, C_{sa}, \) and \( S \) on the particle size distribution and other characteristics are shown in Figures 4–9.

3.2.1. Effect of \( R \). The effect of water–AOT molar ratio \( R \) is shown in Figure 4. The following values were fixed: \( n^* = 2, S = 0.1 \text{ M}, \) and \( C_{sa} = 0.1875 \text{ M} \). The value of \( R \) is changed by varying the total volume of water in the system. On the basis of simple geometric considerations, varying \( R \) changes \( M_{tot} \) and \( N_{agg} \) as follows:

\[
M_{tot} \propto \frac{1}{R^2} \quad (8)
\]

\[
N_{agg} \propto R^2 \quad (9)
\]

The water core volume changes directly in proportion to the change in \( R \). This is compatible with the experimentally observed fact that the water core radius increases with \( R \). This increase has been reported to be linear in the case of the AOT–water–isoctane system.
polydispersity can be seen from experimental investigations. As the salt concentration is increased, the fraction of micelles containing free metal atoms decreases. Further increase in salt concentration leads to an increase in the number of nuclei as well as the final number of particles containing micelles. These results are shown through Figures 6 and 7.

An observation made from Figure 6 regarding the effect of $n^*$ is the apparent disappearance of the minimum in $d_{p,av}$ or $z_{av}$ when $n^*$ is increased from 2 to 5. The reason could possibly lie in the fact that as $n^*$ is increased, the free metal atom population also increases. In the present case, this relatively large free metal population seems to have formed more new nuclei and particles closer to the critical nucleus size, during the exchange process. The average size, over the simulated range of $C_{sa}$, therefore, does not vary much. Also, with an increase in salt concentration, the range of particle sizes increases since the lower end of the particle size is fixed at $d_{p,av}$, while the higher end increases. The polydispersity in particle size is therefore greater at higher salt concentrations.

Figure 8 shows the effect of salt concentration on some important micelle population fractions of physical relevance. These quantities are related by the overall conservation relations, the conservation relations between the distributions at the end of stages I and II. The final fraction of micelles containing metal particles steadily increases with $C_{sa}$, while the final fraction of empty micelles accordingly decreases so that the total micelle population, which is function of only the surfactant concentration, remains constant. The fraction of micelles containing free metal atoms goes through a maximum in the simulated range. The reason for this being that at low salt concentrations the free metal atoms are few and their number increases with more salt. At a particular salt concentration, the balance between formation of nuclei and free metal atoms is achieved. Further increase in salt concentration leads to an increase in the number of nuclei initially formed immediately after the intramicellar reaction. The micelles will therefore contain less free metal atoms and more metal nuclei. This behavior is also translated into the variation of the micelle population in which new nuclei are formed during the exchange process, since the new nuclei are formed from the free metal atoms coming together in the transient micelle dimer.

---

3.2.2. Effect of Salt Concentration. Figure 5 shows the effect of total salt concentration in the microdispersed system on the particle size distribution. The values of $n^*$, $S$, and $R$ are kept at 2, 0.1 M, and 8.35, respectively. An increase in the salt concentration without a change in the number of micelles gives an increase in $d_{p,av}$. As would be expected, and conforming to experimental observations, there is an increase in the average and the maximum particle sizes with salt concentration.

As the salt concentration is increased, the shape of the size distribution curve changes from purely decreasing to one which has a local maximum. The maximum is attained due to the strong effect of the Poissonian distribution. Increase in salt concentration weakens $n^*$, since a smaller number of free metal atoms are formed. This lowering in free metal, for increase in salt concentration beyond a particular value, lowers the formation of nuclei at size corresponding to $n^*$ (critical size). Thus the maximum from the Poissonian distribution is maintained, responsible for the maximum of the final distribution. Crossovers of the distribution curves can be observed when the salt concentration is increased from low to higher values. Higher salt concentrations give larger fractions of micelles with higher metal occupancy numbers. Similarly, the lower occupancy numbered micelle population decreases as the salt concentration is increased, due to a shift in the peak of the size distribution further to the right of $n^*$ at the end of the reduction reaction along with the effect of a decrease in the free metal atom population.

The number of water cores containing minimum number of metal atoms needed for nucleation is small when the salt concentration is low. The number of free metal atoms available for nucleation as well as for particle growth is also small. With an increase in salt concentration, the number of initial nuclei for the reduction reaction increases, and the number of free metal atoms for particle growth decreases. Therefore a minimum in the average particle size is attained at a particular value of the salt concentration. Further increase in salt concentration leads to an increase in the number of nuclei as well as the final number of particles containing micelles. These results are shown through Figures 6 and 7.

---

shown, the distribution peak is at conditions (for is increased. The average size increases from 1.11 nm and the maximum particle sizes increase as Figure 10. The simulations were carried out at nucleation number parameter in the model, used in this study, is the critical water/AgAOT/isooctane system. To an increase in the number of Ag particles formed in the increase in total AOT concentration, at constant parameters for the final particle size. The critical nucleation size and size distribution. The curves here, for S values of 0.1, 0.05, and 0.025 M, are similar to those in Figures 4 and 5, as the $\mu_S$ values are the same. A decrease in the surfactant concentration leads to an increase in average and maximum particle sizes. Keeping other parameters fixed, the effect of a decrease in $S$ is an increase in the aqueous core size and the local water pool salt concentration. Keeping $R$ constant, while increasing or decreasing $V_{aq}$ and $S$ proportionally, the proposed model predicts a constant aqueous core volume (eq 6) for $S \gg CRMC$. The size distribution and the average particle size are unaffected if $S$ is increased at constant $R$, which is again in agreement with experimental findings on average particle sizes. The number of particles however increases and is more, as more micelles can host particles. This feature has been observed experimentally, where an increase in total AOT concentration, at constant $R$, leads to an increase in the number of Ag particles formed in the water/AgAOT/isooctane system.

3.3. Parametric Sensitivity Analysis for the Effect of Critical Nucleation Number. The only adjustable parameter in the model, used in this study, is the critical nucleation number $n^*$. The effect of $n^*$ is shown in the Figure 10. The simulations were carried out at $C_{sa} = 0.1875$ M, $R = 8.35$, and $S = 0.1$ M. For each of the curves shown, the distribution peak is at $n^*$, since for this set of conditions $n^*$ is effectively much greater than $\mu_S$. The average and the maximum particle sizes increase as $n^*$ is increased. The average size increases from 1.11 nm (for $z_{av} = 3.05$) for $n^* = 2$ to 1.61 nm ($z_{av} = 9.31$) for $n^* = 6$, the reason being an increase in the minimum particle size and the availability of more free metal atoms for enhancing particle growth. The particle size distribution is found to be quite sensitive to variation in $n^*$, indicating that this parameter is important and has to be chosen carefully based on experimental data and/or an appropriate nucleation theory.

The fraction of particles having a particular size increases as $n^*$ is increased since more free metal atoms would be available for particle growth. The polydispersity in size also becomes larger as $n^*$ is increased. The explanation for this follows from the fact that for higher $n^*$ more free metal atoms are available for formation of nuclei as well as for particle growth. Another significant observation is the decrease in the fraction of particles having critical nucleus size. The particles would therefore start gathering over wider and the higher size ranges. Therefore for systems in which $n^*$ is high, the conditions of low and moderate salt concentrations should be expected to give highly polydispersed particles.

As $n^*$ increases, whether the number of particles would decrease or increase would be controlled by the competition between particle growth and formation of new nuclei. For the conditions shown in Figure 10, the total number concentration of micelles containing particles, which is the same as the total number concentration of particles, is found to decrease from $5.82 \times 10^{13}$ m$^{-3}$ for $n^* = 2$ to $2.95 \times 10^{12}$ m$^{-3}$ for $n^* = 4$ to $1.73 \times 10^{12}$ m$^{-3}$ for $n^* = 6$. With respect to the model presented here, it is thus seen that the farther $n^*$ is from $\mu_S$ (equivalently, the greater the free metal atom population), the greater the number of free metal atoms and the smaller the total number of nuclei formed during reduction. At the end of intermicellar exchange the free metal atoms contribute more to particle growth rather than to formation of new nuclei. Therefore it is also seen from Figure 10 that the final particle size is closer to $d_p^*$ after growth, where $d_p^*$ is the critical nucleus size.

4. Conclusions

The following conclusions have emerged from this study.

1. A stochastic model for describing the effects of intermicellar exchange process on the ultrafine particle formation in reverse micellar systems has been presented. The approach is physically consistent and computationally efficient.

2. A new contribution made by this model is the formulation of a set of fusion--fission rules to describe the transfer of free metal atoms and metal particles during intermicellar exchange.

3. The results of the model simulations are found to qualitatively predict almost all observed trends known as a function of mixture conditions indicating the important role of intermicellar exchange in the dynamics of the formation of particles in reverse micelles. The simulations using this model can be carried out over a wider range of mixture parametric conditions such as metal salt concentration, surfactant concentration, and aqueous phase to surfactant ratio.

4. The water core size and the critical nucleation number are found to be the primary influencing parameters for the final particle size. The critical nucleation number was found to have a strong effect on the particle size and size distribution.

5. The number of particles formed in most cases was found to be less than the number of micelles. There are three primary reasons for this feature. The salt molecules are distributed according to Poisson's distribution, nucleation occurs beyond a critical number, and metal atoms can be transferred during intermicellar exchange.

Glossary

A. metal salt in kinetic scheme
A. Avogadro constant
CRMC. critical concentration of surfactant molecules for the formation of reverse micelles, assumed to be a well-defined value
$C_{sa}$. total metal salt concentration in the system, based on aqueous phase volume
d$_{av}$. average particle size
d$_p^*$. critical nucleus size (minimum particle size)
f$_p$. fraction of total number of metal particles, of a particle, size (particle size fraction)
k$_{ex}$. second-order intermicellar exchange frequency
k$_{as}$. effective fusion frequency for summation of fusion contributions over the range of indices
k° effective fusion frequency, see eq 10
M free metal species in the kinetic schemes
P metal particles as species in the kinetic schemes
M₀ final total concentration of empty micelles
Mfr total concentration of micelles containing free metal atoms, on completion of salt reduction
Mnew total concentration of micelles having facilitated the formation of new particle nuclei during intermicellar exchange
Mₚ final total concentration of micelles each containing a metal particle
Mₜot total concentration of reverse micelles in the system, based on nonaqueous phase
n* critical nucleation number for metal particle formation
Nagg aggregation number of a reverse micelles
nₚ total number concentration of metal particles in the system, based on bulk phase volume
pₓ probability of a reverse micelle having x molecules
pₓ° initial probability, at t = 0, of reverse micelles having x salt molecules
p₂ probability of a reverse micelle having 2 metal atoms
p₂° initial probability, at t = 0, of reverse micelle having 2 metal atoms
p₂¹ probability of reverse micelles having z metal atoms at the end of stage I
rₚ size (radius) of metal particle formed in a reverse micelle
R total aqueous phase to surfactant molar ratio
R₁ rate of generation of p₂ due to fusion of smaller states, during intermicellar coalescence process
R₂ rate of depletion of p₂ due to fusion of state z with other states, during intermicellar coalescence process
S total concentration of surfactant molecules in the system based on bulk phase volume
Vₐq total volume of aqueous phase
Vₘet atomic volume of metal in liquid phase
Vₐ total volume of nonaqueous phase
Vₚ solid volume of metal particle
x variable denoting nonaqueous phase
xₘax maximum number of metal salt molecules in the aqueous core of a reverse micelle
z variable denoting the number of metal atoms inside a reverse micelle
zₘax maximum number of metal atoms inside a reverse micelle

Greeks
α pseudo-first-order intermicellar exchange rate coefficient
Ω stochastic domain
Ωz stochastic state domain of integral z values
Ωzₑ stochastic state expansion domain of z values
μₓ mean number of metal salt molecules in the aqueous core of a reverse micelle at time t = 0
Φ packing fraction of the solid metal particle

Appendix I
Stochastic-Population Balance Equations. At any time during intermicellar exchange the following equations, formulated for describing the fusion--fission schemes in Figure 2, apply
1. z = 0
\[
\frac{dp₀}{dt} = k° \sum_{2z=1}^{n*} p_z \cdot p₂
\] (10)
where k° = α if z = z ≤ n* - 1 or α/2 if both conditions of z = z and z ≤ n* - 1 are simultaneously satisfied, or α if z ≥ n*.
2. z = 1
\[
\frac{dp₁}{dt} = -αp₁ \sum_{2z=1}^{n*} p_z = -αp₁(1 - p₀)
\] (11)
3. z > 1
\[
\frac{dp_z}{dt} = R₁ - R₂
\] (12)
In eq 12 R₁ is the rate of generation of z from fusion of smaller states, and R₂ is the rate of loss of z due to fusion of z with other possible states. The expressions for R₁ and R₂ for various regimes are
(i) 2 ≤ z < 2n*
\[
R₁ = kₚ \sum_{2z=1}^{n*} p_z \cdot p₂
\] (13)
(ii) 2n* ≤ z ≤ zₘax
\[
R₁ = kₚ(\sum_{2z=1}^{n*} p_z - \sum_{2z=n*}^{zₘax} p_z)
\] (14)
where kₚ = α if z - z = z, or α/2 if z - z ≥ z
(iii) 2 ≤ z < n*
\[
R₂ = -αp₁ \sum_{2z=1}^{n*} p_z
\] (15)
(iv) n* ≤ z ≤ zₘax
\[
R₂ = -αp₁(\sum_{2z=1}^{n*} p_z - \sum_{2z=n*}^{zₘax} p_z)
\] (16)
The expansion domain equations are
(i) zₘax < z ≤ 2zₘax
\[
\frac{dp_z}{dt} = R₁
\] (17)
(ii) zₘax < z < 2n*
\[
R₁ = kₚ \sum_{2z=1}^{n*} p_z \cdot p₂
\] (18)
(iii) z ≥ 2n*
\[
R₁ = kₚ(\sum_{2z=1}^{n*} p_z - \sum_{2z=n*}^{zₘax} p_z)
\] (19)

Acknowledgment. We thank the Department of Science and Technology (DST), India for financial support (DST (III)/2(6)/92-ET) provided for this work. We gratefully acknowledge some good suggestions from one of the reviewers. The assistance of Mr. S. K. Yadav in the final preparation of the revised manuscript is also acknowledged.

LA940584G