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Formation of Catalysts in Inverse Micelles

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Abstract:

We report formation of several small colloidal metal catatlysts in inverted micelle (oil-continuous) systems. These materials have demonstrated catalytic activity *in situ* (i.e. unsupported). The range of solvents possible in this process is large, including all saturated hydrocarbons, cyclic hydrocarbons (e.g. cyclohexane) and aromatics (e.g. toluene, xylene). Three classes of micelle system were investigated, nonionic, anionic, and cationic. Nonionic types allow precise size control but in general do not act as strong stabilizing agents at high temperatures. Cationics can be chosen to provide this permanent stability, providing both charge and steric stabilization. Metal systems formed include Rh, Ni, NiB, MoO_2, Pd, Au and Ag and alloys. Selected examples are given.

Introduction:

Surfactants have many industrially valuable properties and are widely used as wetting agents, emulsfiers etc. One of their most remarkable properties is the ability to allow mixing of otherwise incompatible solvents, e.g. water and oil to form clear homogeneous solutions called microemulsions. This is the basis for their use as tertiary oil recovery agents. For example, the anionic surfactant AOT can solubilize nearly 100 molecules of water for each surfactant molecule in a solution of decane. This talk discusses the use of inverse micelles to solubilize significant quantities of metal salt, which can then be reduced to colloidal metal form by a variety of techniques.

Metal salts are insoluble in oils and consequently techniques of metal colloid formation have focussed primarily on inorganic chemistry in polar solvents such as water. It has been recognized for years that formation of small, narrow size dispersion colloids requires homogeneous nucleation and growth and requires the addition of stabilizers such as polymers to prevent precipitation. In our method, by a suitable choice of solvent and surfactant, we form an inverse micelle system which consists of 1-10 nm size surfactant aggregates called micelles which have nonpolar tail groups forming an interface with the oil-continuous organic phase and polar head groups directed toward the interior of the micelle. The interior of the droplet-like micelle is capable of solubilizing significant amounts of charged metal salts. It also serves as a center for nucleation and growth during the reduction of the metal. Growth of the colloid proceeds by a complex process of collisions between micelles, material interchange, and final stabilization by the surfactant. This growth stage is strongly influenced by the presense of phase boundaries and the strength of interactions between the micelles. These features, properly understood, can be used to control the size and polydispersity of the final product.

Results and Discussion:

This talk discusses the use of nonionic surfactants of the type $CH_3(CH_2)_{i-1}(OCH_2CH_3)_jOH$ (hereafter abbreviated C_iE_j, industrial appelation Brij), the anionic surfactant Sodium-Bis(2-ethylhexyl)sulfosuccinate, (common name AOT), and the cationic surfactant didodecyldimethylammonium bromide, (called DDAB). In contrast to normal micelles which typically have lower critical consolute points in an experimentally accessible range, inverse micelles consist of a single homogeneous phase at high temperatures which separates into two phases as the temperature is reduced. We shall demonstrate how this behavior may be exploited for size control.

In the case of the surfactant family C_iE_j, the ratio of i/j controls the phase separation temperature, since this ratio determines the compatibility of a given surfactant/hydrocarbon system. Low ratios result in high phase separation temperatures, while fixing i/j and increasing

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the length k of the hydrocarbon C_k to make it more hydrophobic will also increase the upper critical consolute point. This allows optimization of solvent/surfactant compatibility during the colloid growth process (e.g. $C_{12}E_3$ with C_{16} or $C_{12}E_8$ with C_8).

We briefly describe the preparation of several metal colloids, illustrating the application of the $C_{12}E_5/C_8$ system. A 5-10 wt% solution of $C_{12}E_5$ is prepared in octane. $NiCl_2$, $Pd(SO)_4$, $RhCl_3$, or $FeCl_3$ can be added **directly** with stirring to a desired metal concentration. Acceptable values lie beween 1 x 10^{-5} and .05 M. The sample is then purged for several minutes with Ar gas. Several methods of reduction are then available, the optimal type depending on metal and solvent/surfactant system. Hydrazine is used in the case of the above metal salts (with the exception of Ni) at a 2x excess. We have established that the reactions are complete under these conditions. In the case of the cationic system DDAB(10 wt%)/toluene the reductant which produces the smallest colloids is generally $NaBH_4$. For other more difficult systems (e.g. $NiCl_2$) we can use Na metal pellets to easily reduce the metal, since we are in a water free system. During this latter process, the solution turns clear nearly instantly, as all the metal is reduced to the zero valance state, but all particles are too small to be in the Mie scattering regime and thus are colorless. Nucleation and growth then occur over a period of 1-5 minutes (depending on metal concentration and solvent/surfactant system) and result in a color characteristic of the colloidal metal, (e.g. red for gold, yellow for silver or Rh, yellow/brown for Pd).

Some metals can be reduced photolytically using either the pulsed third harmonic of a Nd:YAG laser or a CW Argon ion laser operating in the UV at 350 nm. Typical powers are60 mJ or 300 mW respectively and special sample stirring and vial rotation are required to prevent plating out of the metal during the reaction. Examples include Au, Ag, Pt or Ir (when seeded with Ag). Details of this process are beyond the scope of this short talk. Photolytically unstable compounds such as $Fe(CO)_5$ or $Ni(CPD)_2$ can also be encapsulated in inverse micelle systems. Other alloys produced by heterogeneous nucleation (seeding) of one material on another include Pd on Fe, Co/Fe (**figure 1a**), Ir on Ag, and Pt on Au (**figure 1b**).

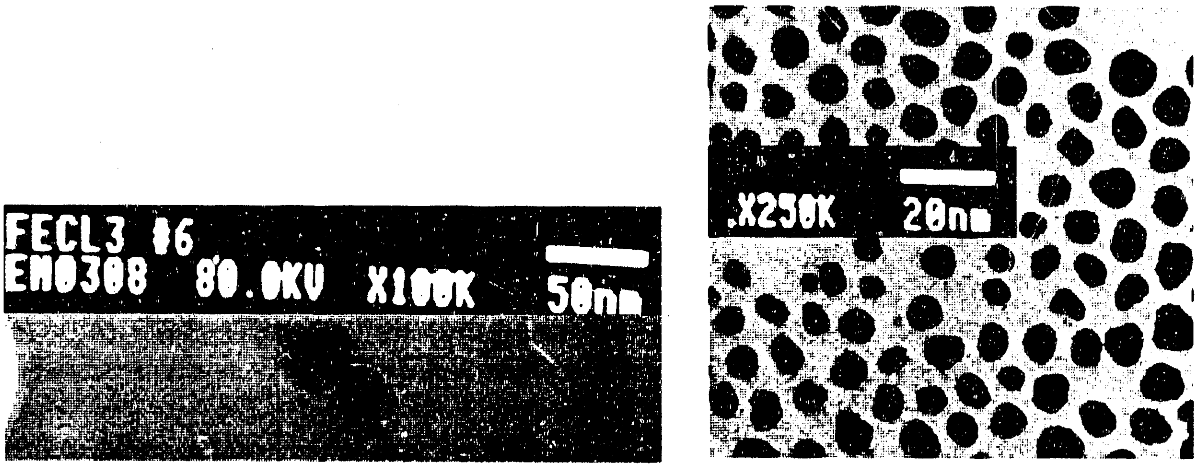
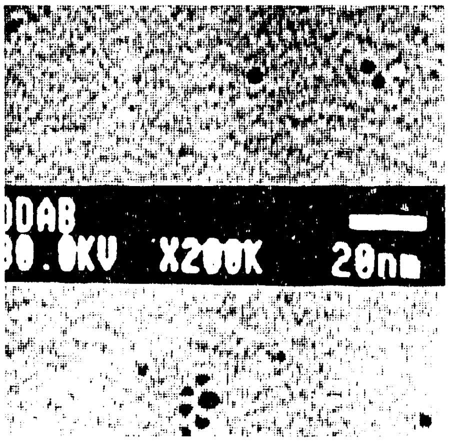


Figure 1a(left),1b(right). TEM of Fe/Co (10:1) and Pt /Au 1:1) bimetallic colloids. The former system was made by heterogeneous nucleation using the $C_{12}E_5(5\%)/C_8$ system, while the Pt/Au was produced by pulsed photolytic reduction in the $C_{12}E_5(10\ wt\%)/C_6$ system.

What are the properties of these small metal colloids with respect to stability, ability to concentrate, temperature, and mixed (complex) solvent mixtures? It should be noted that the latter property is quite important to their use as in situ heterogeneous catalysts. For Pd colloids prepared in the DDAB/toluene system described above the stability is phenomenal. For example, DDAB is not soluable in saturated hydrocarbons such as dodecane. Yet, when yellow

Pd colloids prepared in DDAB/toluene are diluted 10-fold into a linear hydrocarbon the solution becomes cloudy, the DDAB precipitates out of solution, yet the Pd colloids remain in the hydrocarbon solution. Dynamic light scattering measurements reveal no change in size. This provides a method of extracting the bulk surfactant from the solution along with the ions released during the reaction. The remaining solution consists of truely hydrophobic colloids as can be demonstrated in the following remarkable experiment. A Pd/DDAB/toluene solution is added directly to water. The DDAB forms a milky white lower phase in the water, while a clear yellow (Pd colloid) toluene phase remains on top. The ions, of course, follow the surfactant into the lower phase. Drying results in a Pd powder which is redispersable in aromatic, cyclic ,and saturated hydrocarbons. Its size is shown in **Figure 2a**. **Figure 2b** shows the Ni colloid system prepared in a similar way. Size control is achieved in the DDAB/toluene system primarily by increasing the ratio of metal to surfactant. Sizes between 3 and 30-40 nm are possible. This system used in hexadecane results in hydrogenation of pyrene at 100 °C with no apparent catalyst degradation or aggregation.



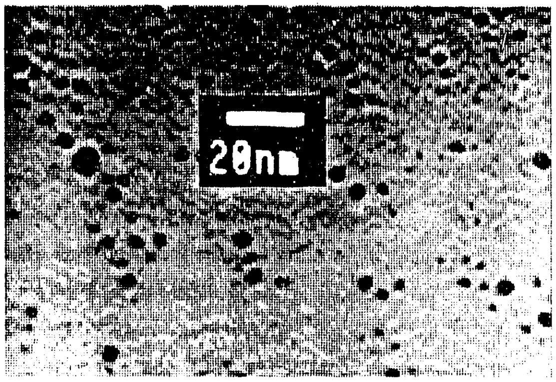


Figure 2a(left), 2b(right). TEM of Pd and Ni colloids produced in the DDAB/toluene system.

The nonionic surfactant systems are much more versatile than the cationic or anonic surfactants since size control via phase behavior is facile, but are not as robust with respect to dilution into foreign solvents. However, this is not a problem since we have formulated stabilizers for all the systems of interest. Because the ratio of i/j can be adjusted for the desired

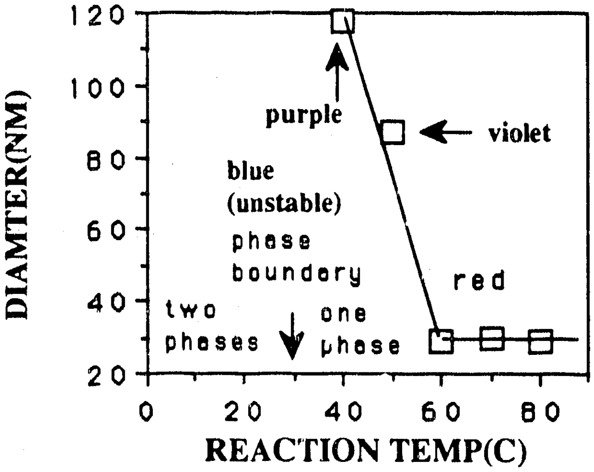


Figure 3. Graph showing Au colloid size variation with reaction temperature in the $C_{10}E_8$/ octane nonioic micelle system. Phase boundary is indicated. Reducing agent is N_2H_4.

solvent system and temperature of reaction. We give a representative example as $C_{10}E_8$(10 wt%)/C_{12}. This system is actually two phase at room temperature, even in the absence of added metal salt. Addition of a metal salt, (e.g. $HAuCl_4$) raises the two phase boundary to ~30 °C at $5x10^{-4}$ Msalt (higher temperatures at higher salt concentrations). Depending on the reduction temperature above this phase boundary various sizes (and colors in the case of gold) can be produced as shown in **Figure 3**. The same principals apply to the other metals mentioned, though the phase boundary positions and desired reaction temperatures vary. Upon lowering the temperature back to room temperature (T=25°C) this system separates into an upper metal colloid phase (clear and red) and a lower surfactant phase (clear and containing the ions). The upper phase may be removed for powder production as with DDAB/toluene.

It is perhaps not surprising that the final metal colloid size closely reflects the micelle sizes found in these systems. This feature guarantees that small size colloids can always be produced, no matter which metal if proper reduction chemistry can be discovered. In the Mo colloid system, for example, very small differences between precursor salt and final reduced metal are observed as shown in **figure 4**. This figure shows a Guinier analysis of the small angle x-ray scattering in the C12E5/C8/MoO2 system. Also shown is the TEM of the colloids which substantiates the size measurements shown.

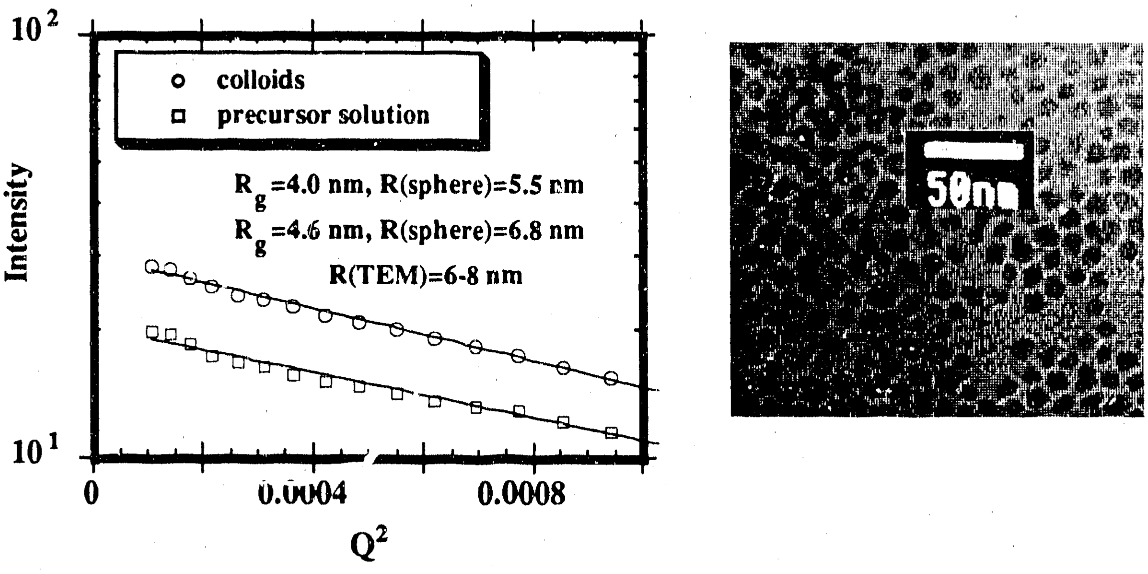


Figure 4. Left graph shows small angle x-ray scattering guinier plot of precursor salt and final MoO_2 *metal colloids in the* $C_{12}E_5$*/octane system while the right TEM shows the particles themselves.*

Micelle systems, because of their complex phase behavior, interactions, and surface active properties, provide a very rich environment for a variety of metal colloid forming reactions. In concluding, we mention two other types of phases in which reactions may be performed, liquid crystalline phases, for example $C_{12}E_6$(50 wt%) in water (hexagonal phase), and also bicontinuous phases (e.g. $C_{12}E_4$(33%)/C_8(33%)/H_2O(33%)).

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