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Preparation of Noble Metal Organosols Containing Polyethylene Glycol Mono-*p*-nonylphenyl Ether

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Synopsis. Stable organosols of ruthenium, rhodium, palladium, and platinum were prepared by evaporating the corresponding noble metal hydrosols containing nonionic surfactant, polyethylene glycol mono-*p*-nonylphenyl ether, followed by dissolving the resulting residues in organic solvents such as chloroform. The organosol of the noble metals was exclusively yielded at a definite range of the surfactant concentration. A mechanism for the formation of the organosols is proposed.

There are fewer reports on the organosols of metals than those on their hydrosols. Svedberg's method is known to be applicable to the preparation of a variety of metal organosols which are somewhat unstable and polydispersed.[1)] Thomas[2)] reported that the pyrolytic decomposition of organometallic compounds such as dicobaltoctacarbonyl in organic media gave monodispersed organosols of the corresponding metals. Hirai et al.[3)] prepared extremely fine colloidal rhodium dispersed in methanol by reducing $RhCl_3 \cdot 3H_2O$ with the methanol in the presence of NaOH. More recently, Boutonnet et al.[4)] proposed a preparative method for colloidal metals in organic solvents from microemulsion. On the other hand, Meguro and Kondo[5)] found that colloidal Fe_2O_3 having positive charge coagulated on addition of sodium dodecylbenzenesulfonate and that the resulting coagulum was redispersed in organic solvents to give an organosol.

In the preceding paper[6)] are reported a variety of noble metal hydrosols stabilized by cationic, anionic, or nonionic surfactant. We have succeeded in converting the hydrosols of noble metals stabilized by nonionic surfactant, polyethylene glycol mono-*p*-nonylphenyl ether, into their organosols. In this paper, preparative procedures and adaptable noble metals and dispersion media are described.

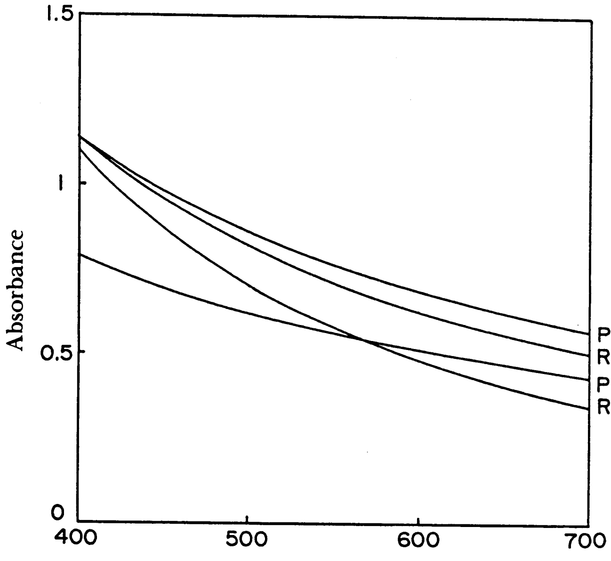

Fig. 1. Visible absorption spectra of noble metal organosols in chloroform (PN conc. in starting hydrosols; 0.01% for Ru and Rh, 0.05% for Pd and Pt).

Experimental

Materials. Noble metal salts used as starting materials were reagent grade $RuCl_3 \cdot 3H_2O$, $RhCl_3 \cdot 3H_2O$, $PdCl_2$, and $H_2PtCl_6 \cdot 6H_2O$. Polyethylene glycol mono-*p*-nonylphenyl ether (degree of polymerization=10, PN) as a protecting agent and sodium borohydride ($NaBH_4$) as a reductant were also of reagent grade. Water was deionized and distilled before use.

Preparation of Noble Metal Organosols. Noble metal organosols were prepared via the corresponding hydrosols previously reported.[5)]

A typical procedure for the preparation of a rhodium organosol is as follows. $RhCl_3 \cdot 3H_2O$ (0.05 mmol) and PN (10 mg) were dissolved in water (95 cm^3). Then, an aqueous solution (5 cm^3) of $NaBH_4$ (0.2 mmol) was poured into the mixture with vigorous stirring. At that time, rhodium ion was rapidly reduced to result in the formation of a clear dark-brown hydrosol of rhodium. The hydrosol was then placed into a Petri dish and heated to evaporate to dryness on a hot plate of a temperature of about 150 °C. A tarry residue left after evaporation was redissolved in chloroform (100

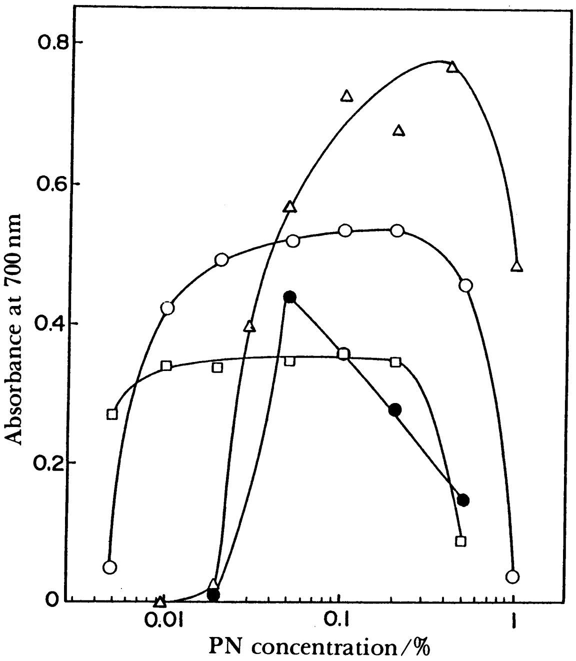

Fig. 2. Absorbance at 700 nm by noble metal organosols in chloroform (○: Ru, □: Rh, △: Pd, ●: Pt).

cm^3) to yield a clear dark-brown sol of rhodium. A small amount of insolble colorless part of the residue was then removed by decantation.

According to a similar precedure, ruthenium, palladium, and platinum sols dispersed in chloroform were obtained. In the case of palladium, NaCl (0.25 mmol) was added to dissolve $PdCl_2$.

Visible Spectroscopy. The visible spectra of the noble metal sols in chloroform were measured on a Shimadzu Model UV-240 spectrophotometer using a cell of a light-path length of 1 cm.

Electron Microscopy. A very small amount of a noble metal sol in chloroform was evaporated to dryness on a thin carbon film supported by Cu-mesh and observed with a Hitachi Model H-800 electron microscope at a magnification of 200000.

Results and Discussion

Hydrosols of ruthenium, rhodium, palladium, and platinum were prepared with varying amounts of PN, and the formation of noble metal organosols from the hydrosols was examined. Thus, the hydrosols were evaporated to dryness and chloroform was added to the residues to dissolve them. In Fig. 1 are shown the typical visible absorption spectra of the supernatant solutions, that is, noble metal organosols. Figure 2 shows the absorbance at 700 nm of the organosols.

Table 1. Solubility of Residues from Noble Metal Hydrosols Left after Evaporation

Solvent	Noble metal, PN(%)			
	Ru 0.01	Rh 0.01	Pd 0.05	Pt 0.05
Chloroform	++	++	++	++
Toluene	++	++	++	−
Ethyl acetate	+	++	++	−
Hexane	−	++	−	−
Acetone	−	−	+	−
Methanol	−	−	−	−

++ Completely soluble, + partly soluble, − insoluble.

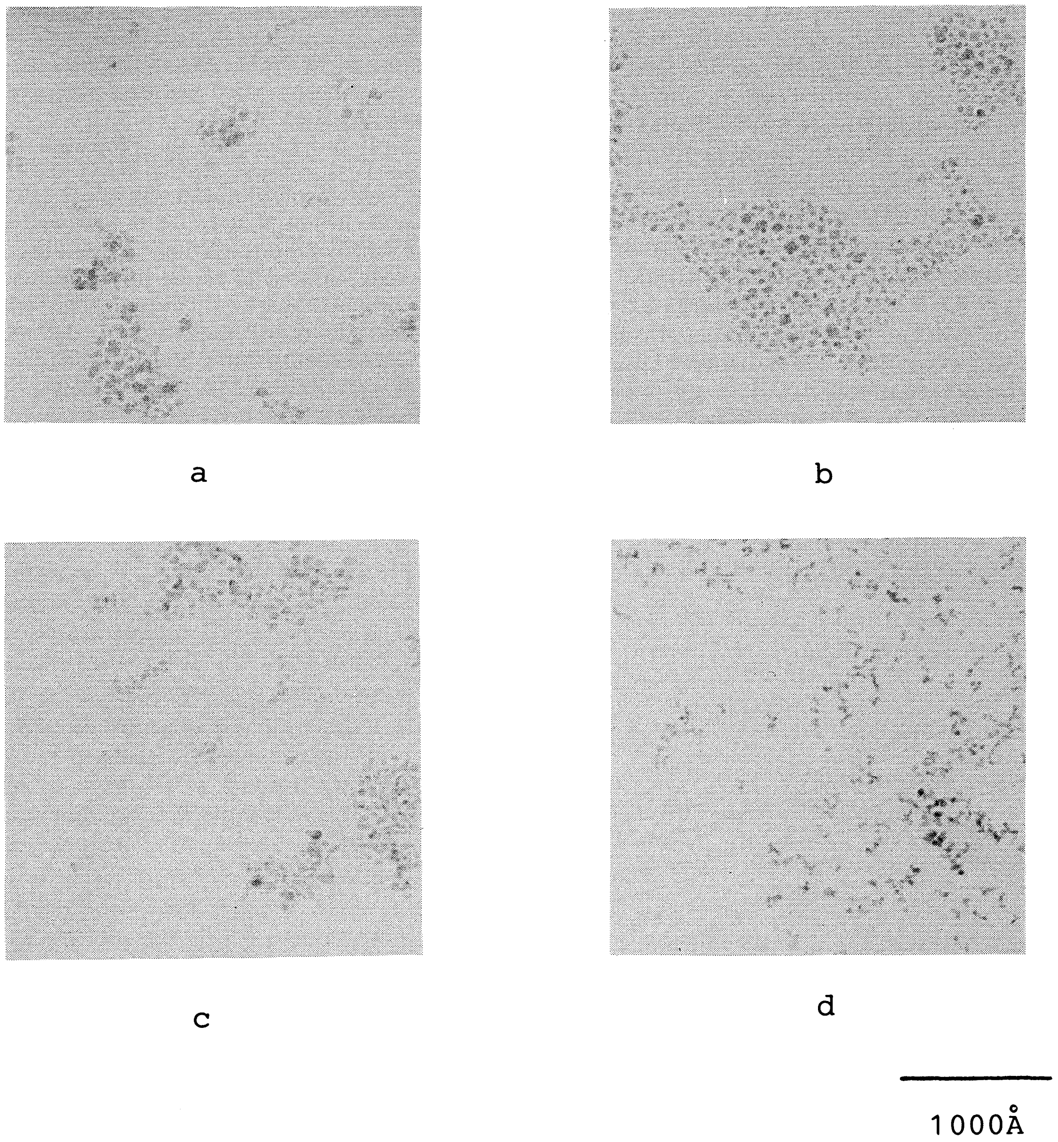

Fig. 3. Electron micrographs of colloidal ruthenium (a), rhodium (b), palladium (c), and platinum (d) from the organosols in chloroform.

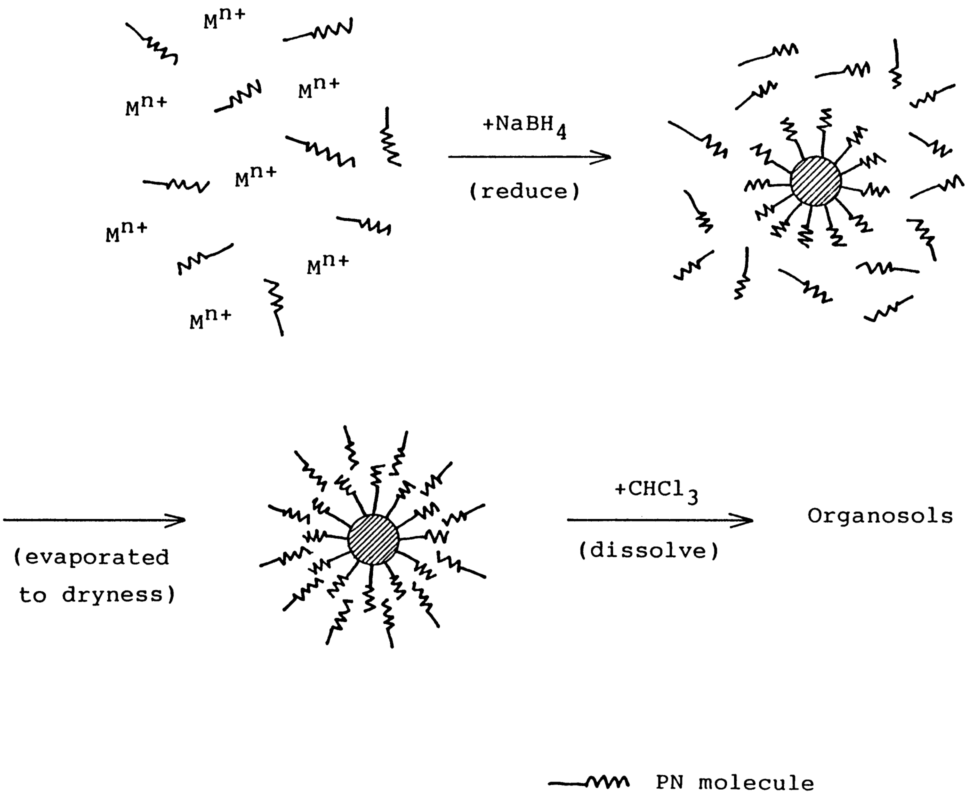

Fig. 4. Mechanism for the formation of noble metal organosols in the presence of PN (∿∿∿ and —— designate the hydrophilic and hydrophobic moieties of PN molecules, respectively).

The absorbance is presumed to be an indication of the amounts of colloidal noble metals in the organosols.[7] This figure indicates that noble metal organosols in chloroform were successfully yielded at a definite range of PN concentration. In other cases, all or a part of colloidal noble metal particles remained in the insoluble residues. Rhodium organosols were obtained at PN concentration of 0.01—0.2% with good reproducibility and were quite similar in color to each other. Ruthenium organosols were also yielded at a wide range of PN concentration. In the case of palladium, larger amounts of PN were required for organosol formation. Among residues from platinum hydrosols, only that from a sol containing 0.05% PN was completely dissolved in chloroform to give an organosol.

In Table 1 are shown the solubilities of the residues from the noble metal hydrosols in a variety of organic solvents. This indicates that chloroform was the most useful dispersion medium for organosols.

Colloidal noble metal particles in the organosols observed by an electron microscope are shown in Fig. 3. Two-dimensional aggregation of the colloidal particles appeared in the electron micrographs might be occurred in the course of evaporation. Such two-dimensional aggregations were also observed in the electron micrographs of the noble metal hydrosols,[6] and the colloidal particles had almost equal dimensions as those in the precursor hydrosols. Narrow spaces lain between the colloidal particles in the aggregates are presumed to correspond to PN layers on the surface of the particles.

A possible mechanism for the formation of noble metal organosols is shown in Fig. 4. At the first step, noble metal ions are reduced with $NaBH_4$ to yield colloidal metal particles. Then the surface of the particles may be immediately covered with PN molecules, of which the hydrophobic moiety orients to the surface. At the second step, excess PN molecules, which exist apart from the surface of the particles, are forced to be attached on the first-adsorbed layers of PN as the evaporation proceeds, and form themselves into the second layer with hydrophobic outer surface. Thus, the colloidal particles could be dispersed in organic solvents.

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