Evolution of gold nanoparticles in micelle by UV-irradiation: A conductometric study

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Evolution of gold nanoparticles from $HAuCl_4$ in a non-ionic surfactant under different experimental conditions, including variable UV flux has been studied conductometrically. The photoproduced Au(0) and its interaction with various ions and dissolution in air are presented, and the results have been substantiated by spectrophotometry.

PARTICLES in the nano-regime have become the most fertile ground of research in the field of science and technology since 1970s. Recent efforts have been directed to design methods for the size-controlled synthesis of nanoparticles for their application in various fields. But a detailed and real-time investigation about the state of metal sol is lacking. The probable reason for this is the need for sophisticated instruments. Here, we have made an effort to study the change in physical properties of metal nanoparticles during evolution and dissolution, without the need for any sophisticated instrument. The physical property we have chosen here is electrical conductivity. It is one of the most sensitive macroscopic properties of solids and solutions. Electrical conductivity of a solution depends on the potential difference between two electrodes, distance of separation between two electrodes, area of each electrode, number of charged components and their mobility. Throughout the study if the first three factors remain the same, then the conductance of the solution will depend on the number of charged components and their mobility. The mobility of the ions depends on their 'effective size'. So a variation in the number of metal particles and their size helps us to study the properties of the solution by conductometric methods. Supporting information has also been put forward from plasmon absorption due to the stabilized nanoparticles in the micelle.

In the recent past several methods have been proposed to prepare gold and silver nanoparticles, e.g. wet chemical reduction[1,2], γ-irradiation method[3–5], laser irradiation technique[6], sonochemical method[7], etc. Recently, it has been reported from our laboratory that UV-activation

technique could be applied successfully to prepare well-defined gold nanoparticles[8,9] from chloroauric acid ($HAuCl_4$) housing in a nonionic micelle, poly(oxyethylene) isooctyl phenyl ether (commonly known as Triton X-100 or TX-100), without the need of any harsh reducing agent. The importance of this method lies in the fact that it is simple and reproducible. The reduction of the metal ion occurs here by the reducing hydroxymethyl radical that is generated by the photolysis of the surfactant, TX-100, by UV-light. Here, TX-100 plays the key role both as a reducing agent (hence its –OH group is oxidized[8,10]) as well as a nanoparticle stabilizer. Stabilization of the particles is rendered by the surfactant because of its capping property[11].

In this communication, we have attempted to interpret the microscopic properties of gold sol, its evolution and reaction in micellar medium. We have prepared gold nanoparticles by UV-photoactivation technique following the method reported earlier[8]. First, the conductance of a set of solutions of TX-100 of varied concentration (10^{-6}–10^{-2} mol dm^{-3}) was measured and a curve was plotted for conductance vs concentration of TX-100 solution. The point of inflexion in this curve denotes the critical micelle concentration (CMC) of the surfactant. Then the fate of the conductometric curve was studied after the formation of gold sol. The gold sol was prepared by addition of a fixed concentration of $HAuCl_4$ (2.7×10^{-5} mol dm^{-3}) to the varied concentrations of TX-100 solutions (as mentioned above) by photoirradiation for 20 min under a flux of 600 lux. Secondly, we have studied the conductance of different concentrations of $HAuCl_4$ (2.7×10^{-5}–9.2×10^{-5} mol dm^{-3}) in TX-100 micelle ($\sim 10^{-2}$ mol dm^{-3}) and the photoirradiated solutions. Photoirradiation was done for 20 min under 600 lux. Thirdly, keeping the flux as well as concentration of TX-100 and $HAuCl_4$ as constant, the effect of the time of irradiation (0–35 min) on the conductometric curve was noted. Fourthly, variation in flux (100–850 lux) was studied keeping the concentration of TX-100, $HAuCl_4$ and the time of irradiation constant. Finally, the effect on conductance as a result of dissolution of Au(0) by cyanide ion (cyano complexation of Au indeed!) has been elucidated. At times, the evolution of gold particle was authenticated through the absorption measurement at 523 nm (λ_{max} of the gold sol).

Photochemical reaction was carried out in 50 ml quartz beaker with a UV-photoreactor (Sankyo, Denki, Germicidal lamp, UVC G8 T5, Japan), with an attachment of changeable flux density (100–850 lux). The beaker was kept at a distance of 3 cm from the light source. The flux density was monitored using a Digital Lux Meter (model LX-101) Taiwan. All the conductance measurements were done with the help of a direct reading conductivity meter (Systronics, India). Absorbance measurements were carried out in a Shimadzu UV-160 digital spectrophotometer using 1-cm quartz cuvette. Cryo-TEM image

was taken using Hitachi S-4300; accelerating voltage, 100 kV.

All the reagents were of AR grade. TX-100 and $HAuCl_4$ were purchased from Aldrich and were used as obtained from the manufacturers, without any further purification. Double-distilled water was used throughout the experiment. Aqueous TX-100, 10^{-2} mol dm^{-3}; $HAuCl_4$, 5.0×10^{-3} mol dm^{-3}, sodium cyanide, 10^{-2} mol dm^{-3} and sodium chloride were used as stock solutions.

In dilute aqueous solution, generally less than 10^{-4} mol dm^{-3}, the behaviour of non-ionic amphiphilic substances almost resembles that of simple organic molecules. At higher amphiphile concentrations, a pronounced deviation from 'ideal' behaviour in dilute solution occurs. At a particular concentration, the surfactant molecules began to form micelle and this particular concentration of the surfactant is known as CMC. At CMC, some of the physical properties such as interfacial tension, electrical conductivity, electromotive force, pH, transport properties, etc. of the solution change[12].

We prepared five sets of aqueous solution of TX-100 of varying concentration (10^{-6}–10^{-2} mol dm^{-3}) and measured their conductance taking 15 ml portion of each solution in a direct-reading conductivity meter. Then a plot of conductance vs concentration of TX-100 was made as shown in curve (a), in Figure 1. The concentration of TX-100 solution corresponding to a maximum conductance in this curve represents the CMC (2.0×10^{-4} mol dm^{-3}) of the surfactant. The pK_a of ethylene glycol is 14.8; it should be about the same for TX-100. Acid dissociation value of a compound is responsible for its increase in conductance (hence there is a slow increase in conductance below the CMC), and presumably the acid dissociation decreases above the CMC (hence there is a fall in conductance value)[13]. Then 80 µl of 5.0×10^{-3} mol dm^{-3} $HAuCl_4$ solution was added to TX-100 solution of varied concentration and the resulting mixtures were photoirradiated for 20 min under 600 lux. It was seen that for a particular flux and concentration of TX-100 and $HAuCl_4$, the conductance rises with irradiation time (up to 20 min) but the variation in flux density (100–850 lux) does not produce any change in the conductivity. The reproducibility of the method in relation to conductivity value with a particular irradiation time has been observed to be excellent. Hence an irradiation time of 20 min and a flux density of 600 lux were chosen. On photoirradiation, the gold(III) solution turned pink. Absorbance measurement of the pink solutions showed the characteristic λ_{max} at 523 nm indicating the formation of Au(0) sol[8]. TEM studies of the gold sol solution on carbon-coated copper grid showed that the size of the particles was ~ 5 nm (ref. 14). Cryo-TEM studies of the frozen solution revealed that the micelle wrapped well-defined Au(0) nanoparticles (Figure 2), which was not observed during normal TEM measurements. The photo-oxidation of phenol or alcohol is known in synthetic organic chemistry. TX-100 has a primary hydroxyl function which, upon photoirradiation, generates hydroxymethyl radical and can thus act as a reducing agent for Au(III) system to form a pink gold sol[15]. This could be corroborated from the fact that gold particles were not produced in aqueous medium in the absence of TX-100. Conductance measurement of each of these pink solutions showed an interesting phenomenon as seen in curve (b), Figure 1. In curve (b), for a lower concentration of TX-100 below its CMC, the conductance rises, but for the higher concentration range the conductance remains almost the same, i.e. after the
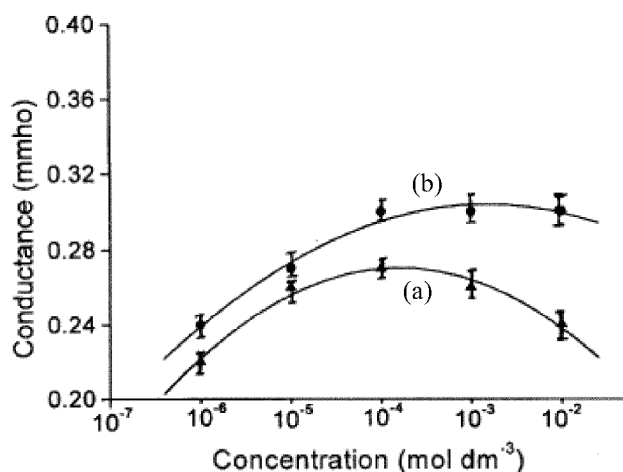

Figure 1. Graphical representation of conductance of 15 ml portion of different concentrations (10^{-6}–10^{-2} mol dm^{-3}) of aqueous solution of TX-100 (curve (a) and after adding 80 µl $HAuCl_4$ (5.0×10^{-3} mol dm^{-3}) followed by photoirradiation for 20 min under a flux density of 600 lux in varying concentrations (10^{-6}–10^{-2} mol dm^{-3}) of TX-100 solution (curve (b)).

Figure 2. Cryo-TEM image of Au nanoparticles of ~5 nm size. Conditions: [TX-100] = 9.9×10^{-3} mol dm^{-3}, [$HAuCl_4$] = 5.0×10^{-6} mol dm^{-3}, Flux density = 600 lux, Irradiation time = 20 min.

CMC, a constant value in conductance was noted. Upon photoirradiation, the chloride ions are released from the complex $[AuCl_4]^-$ ion and since the $HAuCl_4$ concentration is fixed, the number of free Cl^- ions in each solution is expected to be the same. Thus it is expected that nature of the curve (b) should be similar to curve (a) in Figure 1. But, in practice, is not so. A plausible explanation for this may be formulated as follows.

Under a definite flux density for a particular concentration of $HAuCl_4$ solution and fixed irradiation time, as the concentration of TX-100 increases the number of Au(0) particles increases with consequent decrease in size of the particles[9]. Though, at first sight, the number of free Cl^- ions seems to be the same, it will differ from one set to another if the electrolytic effect is taken into account. When the number of gold particles increases, the total available surface area (considering all gold particles) also increases and therefore, more number of Cl^- ions get adsorbed onto the surface of gold particles. Due to this, the particle surface becomes negatively charged and should make a contribution to the measured conductance of the solution. Hence as the number of particles increase, the conductance value increases. But after the formation of the micelle, presumably, the remaining Cl^- ions become incorporated in the micelle and the mobility of the ions is somewhat retarded. To check the effect of Cl^- ions on conductance in the micelle, two sets of experiments were performed. The successive addition of Cl^- as NaCl solution (10^{-2} mol dm^{-3}) to the aqueous as well as micellar solutions (TX-100) indicates a slower increase in the conductance value in the latter case (Figure 3 a). A similar effect was also observed when the above experiment was done taking the preformed gold particles into consideration (Figure 3 b). Thus, in the micelle there are two key factors for the observed conductance value. The increased number of Au(0) particles tends to increase the conductance value (electrolytic effect). On the other hand, the mobility of Cl^- ions becomes restricted in the micelle. As a result of the embedded Cl^- ions in the micelle, the conductance value is diminished and as a compromise, constancy in the conductance value was noted.

Aqueous solution of TX-100 shows conductance because of its probable dissociation (due to the presence of $-OH$ functionalities in TX-100) in solution, as discussed earlier. Addition of $HAuCl_4$ solution, even at the trace level ($\sim 10^{-5}$ mol dm^{-3}), showed further enhancement in conductivity due to the presence of H^+ and $[AuCl_4]^-$ ions, as seen in curve (a), Figure 4. Now, if the solution is irradiated under flux of 600 lux, the conductance of the solution is found to increase further. It is seen that for a fixed surfactant concentration, with the increase in concentration, of $HAuCl_4$ solution, the conductivity is increased. This is represented in the curve (b), Figure 4. The rapid rise in curve (b) compared with the curve (a) could be accounted for by the generation of free Cl^- ions
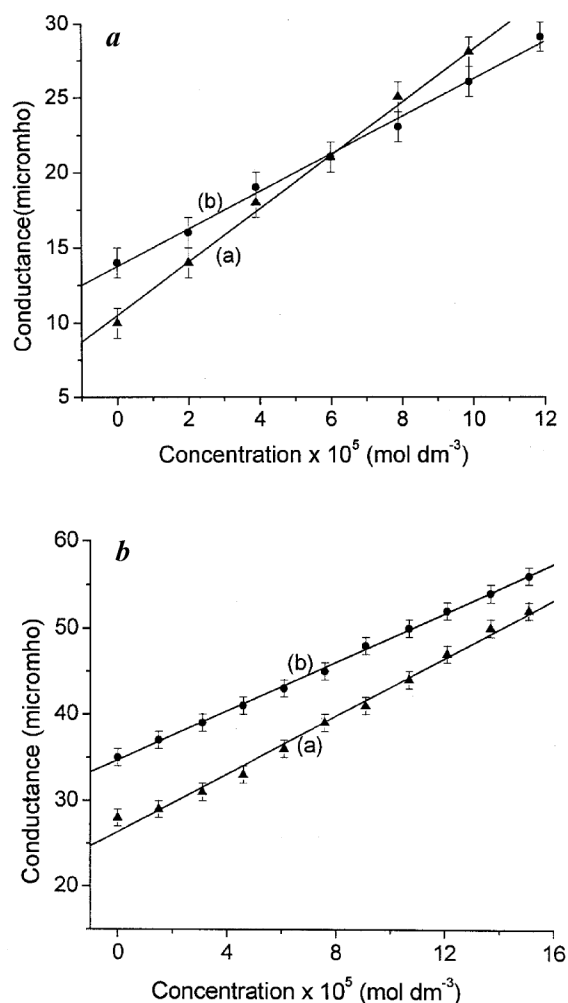

Figure 3. Conductometric studies upon addition of NaCl in aqueous (curve (a)) and TX-100 (curve (b)) media in (*a*) Absence of gold nanoparticles, and in (*b*) Presence of gold nanoparticles. Conditions: [TX-100] = 7.7×10^{-3} mol dm^{-3}, [Au] = 1.8×10^{-5} mol dm^{-3}.
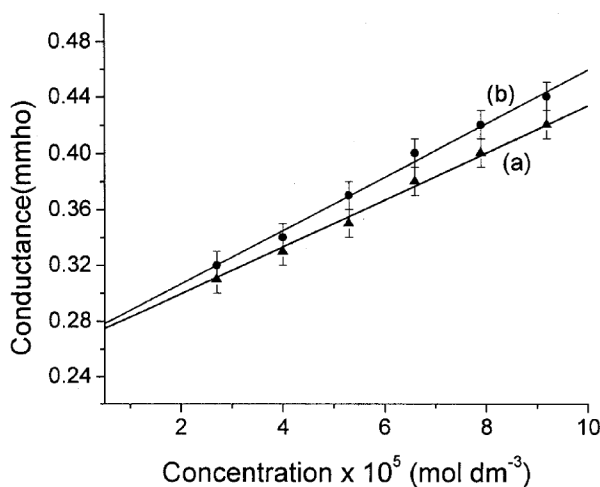

Figure 4. Graphical representation of conductance of varying concentrations ($2.7 \times 10^{-5} - 9.2 \times 10^{-5}$ mol dm^{-3}) of $HAuCl_4$ in TX-100 ($\sim 10^{-2}$ mol dm^{-3}) micellar medium before irradiation (curve (a)) and after irradiation for 20 min under flux density 600 lux (curve (b)).

and their electrolytic effect on gold. Presumably, the latter effect would contribute a little to the conductance value. As the concentration of $HAuCl_4$ increases, the number of Au(0) particles increases and so the conductance increases.

Now, for a fixed concentration of TX-100 (9.8 × 10^{-3} mol dm^{-3}) and $HAuCl_4$ solution (7.9 × 10^{-5} mol dm^{-3}), the irradiation time was varied under a flux of 600 lux. It was seen that from the beginning up to 20 min time, the conductance increases, after which it became a constant (Figure 5). When the time of irradiation increases, the number of gold particles increases and simultaneously the number of free chloride ions also increases. The conductance also increases due to chloride ions (though their mobility is somehow retarded by the micelle) and their consequent electrolytic effect. The complete generation of gold nanoparticles needs ~20 min irradiation and hence the maximum conductance value is observed after 20 min. There is a regular increase in the plasmon absorption value upon irradiation up to 20 min of a solution containing $HAuCl_4$ in TX-100 micelle (shown in curves (a–d) in Figure 6). On prolonged irradiation of the solution there is a blue shift of the λ_{max} values with a shrinkage in the integrated absorption curve (see curve (e), Figure 6), presumably due to inter-particle charge distribution[16] causing particle disintegration. However, change in size could not be ascertained explicitly from the conductometric experiments as there remains no scope of generation of new ions which might contribute to the conductance value.

To study the effect of flux density on conductance, the flux density was varied from 100 to 850 lux keeping other parameters, i.e. concentration of TX-100, concen-
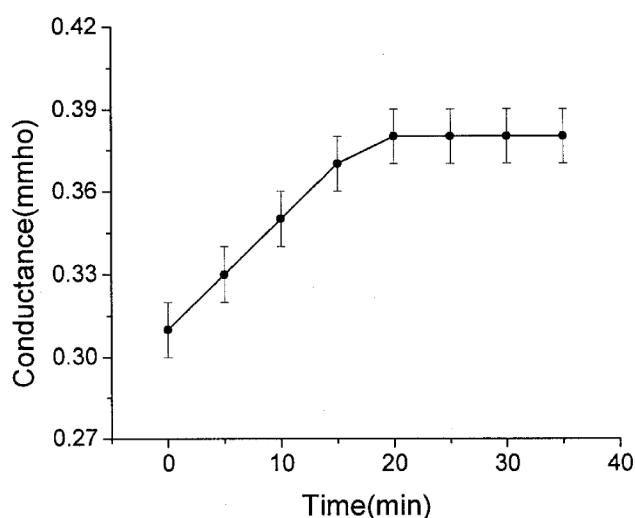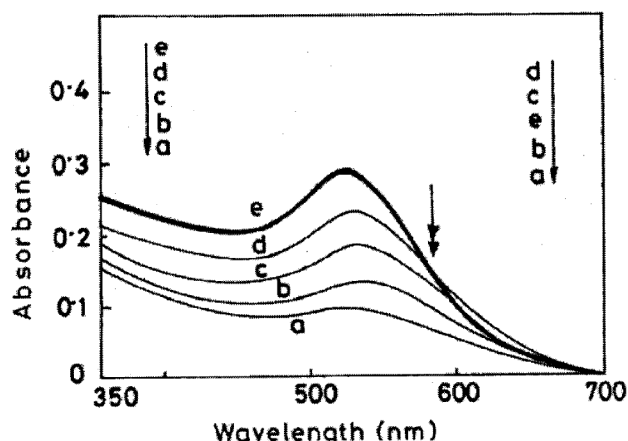

Figure 6. Absorption spectra of the successive generation of gold nanoparticles in TX-100 micelle for different times of irradiation (0–35 min). Conditions: [TX-100] = 9.8 × 10^{-3} mol dm^{-3}, [HAuCl$_4$] = 7.9 × 10^{-5} mol dm^{-3}, Flux density = 600 lux.

tration of $HAuCl_4$ and irradiation time as constant. Variation in flux density did not change the conductivity of the experimental solution.

Lastly, the effect of addition of NaCl and NaCN on the conductivity of the solution containing photoproduced Au(0) particle in the micelle was studied. It was observed that for a particular concentration (7.9 × 10^{-5} mol dm^{-3}) of Au(0) sol, if NaCl solution (10^{-2} mol dm^{-3}) is added successively, then the conductance remains constant, but addition of NaCN (10^{-2} mol dm^{-3}) causes a decrease in conductivity of Au(0) sol. From the absorbance measurement, it has been seen that the absorbance value decreases successively with successive addition of NaCN solution. Under ambient condition, gold nanoparticles are dissolved by the cyanide ion[17,18]. The dissolution reaction is

$$4Au(0) + 16NaCN + 6H_2O + 3O_2 \rightarrow$$
$$4Na[Au(CN)_4] + 12NaOH. \qquad (1)$$
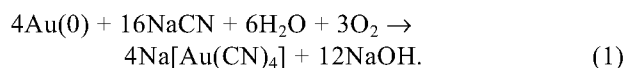
The ion $[Au(CN)_4]^-$ contains square-planar Au(III) and the complex exhibits back-bonding with the filled 5d orbital of gold and vacant π^* orbital of the cyanide ligands[19]. Recently, it has been shown that gold particles could be generated from this cyano complex of gold[20], for a gold concentration up to 7.1 × 10^{-5} mol dm^{-3} and cyanide concentration up to 3.3 × 10^{-5} mol dm^{-3}. The steep decrease in conductance can be explained as follows: Au(0) sol in aqueous TX-100 micelle contains H$^+$ and Cl$^-$ ions. When NaCN is added to this solution, NaOH is formed. This is equivalent to the replacement of H$^+$ ion by Na$^+$ ion. The mobility of Na$^+$ is several times less compared to H$^+$ ion. Hence the conductance decreases steeply. This was also proved by adding NaOH (10^{-2} mol dm^{-3}) to the Au(0) sol. When NaOH is added successively to the Au(0) sol, the conductance value was

Figure 5. Graphical representation of conductance of HAuCl$_4$ in TX-100 for different times of irradiation (0–35 min) under a definite flux density. Conditions: [TX-100] = 9.8 × 10^{-3} mol dm^{-3}, [HAuCl$_4$] = 7.9 × 10^{-5} mol dm^{-3}, Flux density = 600 lux.
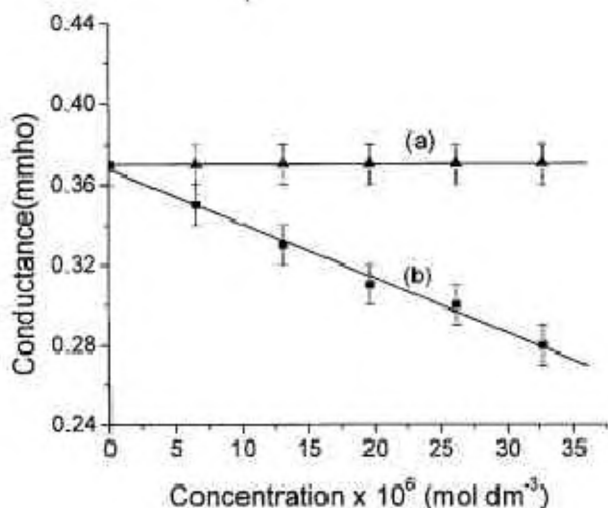
Figure 7. Graphical representation of conductance of Au(0) in TX-100 micelle with successive addition of NaCl solution (curve (a)) and NaCN solution (curve (b)). Conditions: [TX-100] = 9.8×10^{-3} mol dm^{-3}, [Au(0)] = 7.9×10^{-5} mol dm^{-3}.

also found to decrease. Upon UV-irradiation, a set of HAuCl$_4$ solutions in TX-100 micelle did not change their respective conductance values with the addition of NaCl (10^{-2} mol dm^{-3}) solution. This is due to the binding of free chloride ions in the micelle. This is the reason that addition of NaCl in the vessel of gold nanoparticles did not change the conductivity. The effect of addition of NaCl and NaCN is shown in Figure 7.

This is a simple depiction of the macroscopic property of nanoparticles. The observation helps authenticate the formation of gold nanoparticles in the micellar medium by conductometry supported through plasmon absorption measurements. The stepwise evolution of Au(0) could be determined from the photoactivation process. The adsorption of ions onto the particle surface and the reaction, i.e. dissolution in particular, under ambient condition are demonstrated.

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Assessment of changes in water-hyacinth coverage of water bodies in northern part of Bangalore city using temporal remote sensing data

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Indian Remote Sensing Satellite (IRS) LISS-II and III images of different years/seasons (1988–2001) were used to compare the water-covered areas and the water hyacinth-covered areas of six water bodies (Doddabommasandra, Yelahanka, Jakkur, Rachenahalli, Nagavara and Hebbal) in and around the northern parts of Bangalore city, Karnataka, India, giving the exact areas under hyacinth cover. The findings showed that the area under water-hyacinth cover has increased in recent times compared with previous years. One possible reason for this is the pollutants being let into the water body, having excess nutrients which are absorbed by water hyacinth thus increasing the area under cover. The growth of water hyacinth is

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