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Pulse radiolytic studies of metallic clusters in a quaternary microemulsion system

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Abstract—The radiation-chemical reduction of Tl^+, Co^{2+} and Ni^{2+} ions in water-in-oil microemulsion has been described. Rate constants for the reduction of the metal ions by e_{aq}^- were found to be much lower compared to those in aqueous solution. The absorption spectrum and the rate constants of formation of the transient intermediates of metal clusters were correlated with the water-pool size, surrounding environment and compared with data in aqueous solution. Tl_2^+ reacts with Cd^{2+} with $k = 1.1 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$. Reactions of Tl_2^+ and Co^+ with Ag^+ leads to the formation of Ag metal particles. No reaction was observed from Cd^+ to Tl^+ or Co^{2+}. The results are discussed in terms of dynamic exchange of materials between the polar cores of microemulsion. This exchange facilitates formation of silver particles.

INTRODUCTION

Metal nanoparticles are now being used in many applications, such as photography, catalysis, etc. [1–4]. Various techniques have been employed for preparing metal nanoparticles [5–14]. It has been shown that the size and shape of the particles can be controlled by changing the concentration of the capping material and metal ion concentration [10]. Recently, micelles, reverse micelles and microemulsions have attracted considerable attention for preparation of nanoparticles. It has been suggested that one can control the shape of the particles in such systems [15, 16].

A reverse micellar system and water-in-oil microemulsion is an optically transparent, thermodynamically stable dispersion of two relatively immiscible liquids consisting of micro-domains of one or both liquids, which are stabilized by an interfacial film of surface-active molecules. The size of the water droplets is determined

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by the composition of the medium, that is, by w_o, which is the molar ratio of water to surfactant [17]. These water droplets can be used as microreactors for preparing metal particles. The growth processes of metal particles are constrained by the surfactant molecules surrounding the water droplets. Much of the reported work on metal nanoparticles in microemulsion is done by chemical reduction [16, 17]. To understand various intermediate processes involved in the formation of nanoparticles, it is important to understand the mechanism of their formation. In aqueous solution, using a radiolytic technique, these processes are well understood [5–14] and one can not presume much difference in microemulsion as the reaction process takes place in aqueous environment. Nevertheless, there exists a possibility of difference as the water droplets in microemulsion do not have a continuum. In addition to this, due to the difference in the process of generation of reactive species (*vide infra*), the rates of reaction may get affected. This may have important biological consequences, as microemulsion mimics the conditions prevailing under biological environment. The study of reduction of metal ion in microemulsion may also throw some light on redox processes in metal proteins. Pulse radiolysis has proven a useful tool for investigation of the mechanism of the processes involved in formation of the metal nanoparticles [5–14]. In the present work, the microemulsion used was composed of cyclohexane/sodium lauryl sulfate/1-pentanol/water. The abnormal valence states of metals in water core were generated radiolytically and their interaction with various metal ions were investigated. The effect of water-core on the reactivity of e_{aq}^- with metal ions and on their absorption characteristics was also studied.

EXPERIMENTAL

Sodium lauryl sulfate (NaLS) was obtained from SISCO and used as received. Cyclohexane (Spectrochem, India), 1-pentanol (Spectrochem), $CoSO_4$ (BDH), $NiSO_4$ (BDH) and Tl_2SO_4 (BDH) were used as received. All other chemicals used were of either AR or GR grade. Pulse radiolysis was carried out with 7 MeV electrons from a linear accelerator. Pulses of 500 ns were used. The dosimetry was carried out using an air-saturated aqueous solution containing 5.0×10^{-2} M KSCN and $(SCN)_2^{\bullet-}$ was monitored at 500 nm. The absorbed dose per pulse was calculated assuming $G\varepsilon$ for $(SCN)_2^{\bullet-}$ to be 21 520 $M^{-1}\,cm^{-1}$ per 100 eV, where G is the radiation chemical yield expressed as the number of molecules formed or destroyed per 100 eV of energy absorbed and ε is the molar absorptivity. The details of the pulse radiolysis system are given elsewhere [18]. The optical path length of the cell was 1.0 cm. The dose per pulse was 67 Gy. UV-vis ground state absorption spectra were taken on a Shimadzu 160A absorption spectrophotometer.

Microemulsions were prepared by adding nanopure water to NaLS, followed by addition of cyclohexane and 1-pentanol. All microemulsions were bubbled with N_2 prior to irradiation. On irradiation of the microemulsion, the hydrated electrons are produced via the following reactions [19]

$$C_6H_{12} \rightsquigarrow C_6H_{12}^{+} + e^{-} \quad (1)$$

$$H_2O\ (\text{water pools}) \rightsquigarrow e^{-}_{aq},\ H,\ {}^{\bullet}OH,\ H_3O^{+} \quad (2)$$

The H and ${}^{\bullet}OH$ radicals produced are scavenged by pentanol. However, the yield of hydrated electrons in the microemulsion is lower than that in pure water. It increases as w_o increases ($w_o = [H_2O]/[NaLS]$). The details of the system are given elsewhere [8, 20]. To study the electron transfer reaction in the presence of two metal ions, the concentration gradients were chosen in such a way that e^{-}_{aq} explicitly reacted with one metal ion.

RESULTS AND DISCUSSION

Spectra of Tl_2^{+} and Tl^0

The UV-Vis absorption spectra of these two reduced forms of thallium were reported earlier [21–23]. As mentioned earlier, the yields of hydrated electrons in the microemulsion are lower than that in aqueous solution. Therefore, to measure the transient, the concentration of Tl_2SO_4 has to be increased up to 1.0×10^{-3} M. It is known that once Tl^0 is produced, it undergoes reaction with Tl^{+} to give Tl_2^{+} (equation (3))

$$Tl^0 + Tl^{+} \rightleftharpoons Tl_2^{+} \quad (3)$$

Equilibrium constant values between 2.3×10^3 and 1.4×10^2 have been reported for the above equilibrium [22, 23]. In aqueous solution at concentration greater than 2.0×10^{-4} M the equilibrium in equation (3) shifts towards the right. As mentioned earlier, in the microemulsion the reaction takes place in the water pool, so we do not expect any significant difference in the equilibrium constant for reaction (3). Hence, under our experimental conditions, we could not detect Tl^0. The reaction of Tl^{+} with e^{-}_{aq} was monitored at 700 nm. It was observed that the bimolecular rate constant for the reaction of e^{-}_{aq} with Tl^{+} increased as w_o increased. The results are compiled in Table 1. The variation in rate constants can be explained on the basis of ionic strength of the solution. At lower w_o, the local concentration of Tl_2SO_4 is high and therefore the ionic strength is high. As w_o increases, both the local concentration of Tl_2SO_4 and the ionic strength decrease. Hence the bimolecular rate constant for the reaction of e^{-}_{aq} with Tl^{+} increases.

Figure 1 shows the spectrum of the transient obtained in N_2-bubbled microemulsion solution ($w_o = 36$) containing 1.0×10^{-2} M Tl_2SO_4. The spectrum was fully developed at 3 μs after the pulse. On comparing with Tl_2^{+} spectrum in aqueous solution, it was observed that the absorption maximum in the microemulsion is blue-shifted by about 50 nm. No other transient formation was observed on decay of the Tl_2^{+} absorption. In aqueous solution, Tl^0 shows an absorption band at 450 nm

Table 1.
Variation of bimolecular rate constants for the reaction of e^-_{aq} with w_o for various metal ions

Solution	w_o	$t_{1/2}$ (e^-_{aq}) (μs)	G (e^-_{aq})^a	$k_2 \times 10^{-8}$ ($\text{M}^{-1}\,\text{s}^{-1}$) Tl^+	$k_2 \times 10^{-8}$ ($\text{M}^{-1}\,\text{s}^{-1}$) Co^{2+}	$k_2 \times 10^{-8}$ ($\text{M}^{-1}\,\text{s}^{-1}$) Ni^{2+}
1	16	12.1	1.28	0.3	0.64	0.58
2	36	13.1	1.55	4.0	1.40	1.80
3	60	6.5	1.94	37.5	4.50	8.10

^{a} G = number of species per 100 eV.

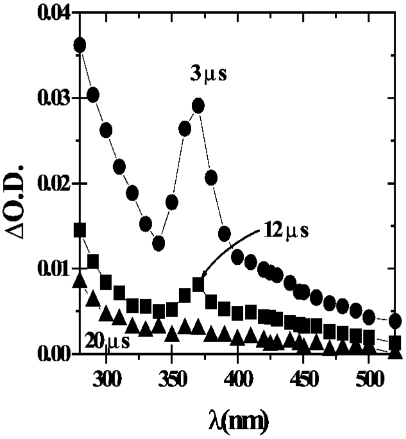

Figure 1. Transient absorption spectrum obtained in N_2-bubbled microemulsion solution (w_o = 36) containing 1.0×10^{-2} M Tl_2SO_4.

[21–23], which corresponds to a photon energy of ~ 2.75 eV. This energy is substantially smaller than the first excitation energy of 3.29 eV of gaseous Tl^0. As stated above we could not determine the absorption spectrum of Tl^0 under our experimental conditions. However, the absorption maximum of Tl_2^+ obtained in the present study corresponds to 3.35 eV, which is much closer to the first excitation energy of Tl^0 in the gaseous phase. It is important to mention here that no significant change was observed in the ground state absorption spectrum of Tl^+ in microemulsion. The observed blue shift in the absorption spectrum of Tl_2^+ could be due to the rigidity of the matrix. As mentioned earlier, in the present microemulsion 1-pentanol is used as a co-surfactant, which results in an increase in the viscosity of the interfacial region and in the water core. This may affect the electron delocalization on absorption of light as surfactant molecules at the surface of the water core further constrain the droplets. Mostafavi *et al.* [24] have shown that the presence of ligands affects the absorption spectrum of Ag^0.

It has been reported that, at a low pentanol/cyclohexane ratio, the system becomes rigid [25]. This affects the exchange between water droplets. This was confirmed by measuring the kinetics of the transient of the solubilized reactant in the water

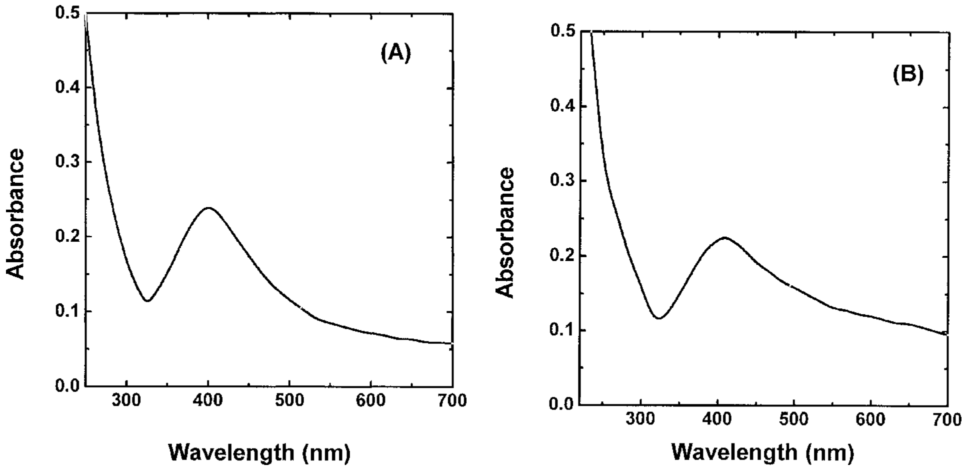

Figure 2. (A) Absorption spectrum of silver metal sol obtained, on irradiation (Dose = 10 Gy), in N_2-bubbled microemulsion solution containing 1.0×10^{-2} M Tl_2SO_4 and 5.0×10^{-4} M $AgClO_4$. (B) Absorption spectrum of silver metal sol obtained, on irradiation (Dose = 10 Gy), in N_2-bubbled microemulsion solution containing 5.0×10^{-3} M $CoSO_4$ and 1.0×10^{-4} M $AgClO_4$.

core. For example, it was observed that the decay of Tl_2^+ showed a first order decay at low w_o. The contribution of second order decay increased with increase of w_o.

On irradiation for longer times (dose = 1×10^4 Gy) of N_2-bubbled microemulsion solution containing 1×10^{-2} M Tl^+, formation of colloidal thallium was not observed. The results obtained can be rationalized by considering the nucleation and growth processes. The process of particle formation after reduction of metal ion by e_{aq}^- can take place once monomers and nuclei required for the formation of particle grow. At the concentration used in the present study, the ion occupancy number in water core is greater than the critical number of monomers. The transient radicals produced can interact with each other or with the parent ions. It seems that the present microemulsion could not stabilize the nuclei required for the particle formation.

On irradiation of microemulsion containing 1×10^{-2} M Tl_2SO_4 and $CdSO_4$ (2.0×10^{-4} M), it was observed that the decay of Tl_2^+ increased. The rate of Tl_2^+ decay was found to increase with increase in the concentration of Cd^{2+}. Thus, it is concluded that Tl_2^+ reacts with Cd^{2+}. The specific rate of the reaction of Tl_2^+ with Cd^{2+} was calculated from the pseudo first order decay of the Tl_2^+ and it was found to be 1.1×10^8 $M^{-1}\,s^{-1}$.

On pulse irradiation of a microemulsion solution containing 1×10^{-2} M Tl_2SO_4 and 5×10^{-4} M $AgClO_4$, it was not possible to determine whether Tl_2^+ reacted with Ag^+ due to overlapping absorption bands of Tl_2^+ with Ag^o. However on irradiation for longer times (dose = 10 Gy) the absorption of Ag metal clusters with absorption band centered on 400 nm was observed (Fig. 2A). This shows that the electron transfer from Tl_2^+ to Ag^+ take place.

Reaction of Co^{2+} and Ni^{2+}

Figure 3 shows the transient absorption spectrum of a microemulsion solution ($w_o = 36$) containing 1.5×10^{-3} M $CoSO_4$ after delivery of an electron pulse. The bimolecular rate constant for the reaction of e^-_{aq} with Co^{2+} was determined at 700 nm. and is given in Table 1. In the case of Co^{2+} also it was observed that as w_o increased the rate constant for reaction of e^-_{aq} with Co^{2+} increased. It can be seen from Fig. 3 that in the case of Co^+ also there is some blue shift (~10 nm) in microemulsion solution compared to the reported absorption bands in aqueous solution. Similar results were obtained for Ni^+. Since no gas phase results are available for Co^+ and Ni^+ the observed results cannot be compared and it is difficult to make a remark on the effect of solvent (surroundings) on the absorption of Co^+ and Ni^+. The bimolecular rate constants at different w_o are given in Table 1.

On pulse irradiation of microemulsion solution containing 5×10^{-3} M $CoSO_4$ and 1×10^{-4} M $AgClO_4$, it was not possible to determine the electron transfer from Co^+ to Ag^+ due to the overlapping of the absorption bands. However, formation of colloidal Ag particles, which showed characteristic absorption at 400 nm, confirms that Co^+ transfers an electron to Ag^+ (Fig. 2B). It can be seen from Fig. 2B that the absorption spectrum of silver clusters is broader compared to that observed with Tl^+. This could be due to the formation of some Co sol, which shows a continuum spectrum at below 500 nm.

Both in the case of Tl_2^+ and Co^+, the absence of any formation of mixed cluster shows that the electronic structure of the monovalent cluster or ion does not facilitate the binding of σ orbital with 5 s orbital of Ag^+.

It has been reported that it is difficult to reduce Co^{2+} ions to the metal at equivalent doses that are sufficient to reduce other divalent metal ions. The redox potential for (Co^{2+}/Co^+) is −1.8 V while standard potential for the couple (Co^+/Co^0) is −2.9 V.

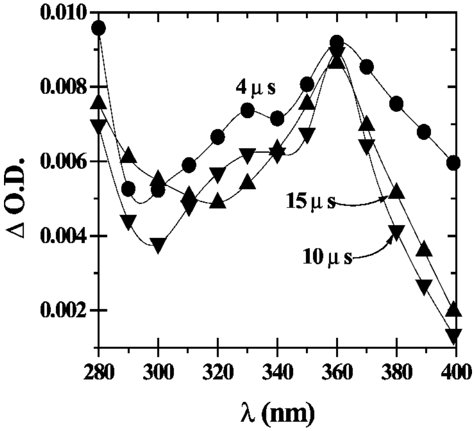

Figure 3. Transient absorption spectrum obtained in N_2-bubbled microemulsion solution ($w_o = 36$) containing 1.5×10^{-3} M $CoSO_4$.

Therefore the disproportionation of Co^+ in reaction (4)

$$Co^+ + Co^+ \rightarrow Co^0 + Co^{2+}, \tag{4}$$

is thermodynamically unfavourable [26]. In fact, as stated earlier, under our experimental conditions, the Co^+ decays by a first order process. This could be one of the reasons for not observing colloidal Co, showing that reduction of cobalt ions by e^-_{aq} is energetically unfavourable.

In addition to unfavourable thermodynamic conditions for the formation of colloidal Co there exists a possibility that the individual clusters of Tl^+ and Co^{2+} are not being stabilized by the interaction with the palisade layer of the microemulsion. This could also be the reason for not observing the formation of Tl and Co particles even on irradiation for longer times (dose $= 1 \times 10^4$ Gy). In the presence of a proper stabilizer it has been shown that Co metal particles can be prepared using γ-radiolysis [7]. Thus, there exists a possibility that the structure of a surfactant can play a role in stabilizing metal particles in microemulsion as has been shown for aqueous solutions. Therefore, a detailed work with different functional groups in the surfactant, which can bind to the metal ion is necessary. Attempts are being made to look into this aspect. At present, it can be said that the present surfactant in the microemulsion offers a good stability for the colloidal particles of noble metals such as Cu [8] and Ag [27].

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