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Stabilization of monolayers by metal nanoparticles manifested in oscillations of interfacial potentials

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Abstract

Stabilization of monolayers at the organic-aqueous interface by citrate protected Au nanoparticles is shown to affect the interfacial dynamics and this effect is manifested in the oscillations of the interfacial potential. Variation in the size and concentration of the nanoparticles systematically affects the oscillations, attributed to particle-induced stabilization of monolayers. A structural model of the monolayer to account for the observed changes is proposed.

Keywords: Stabilization; Monolayer; Organic-aqueous interface

1. Introduction

Interfacial oscillations were first studied in biological systems. Excitation of nervous cells and heart beat were studied extensively to understand their self-oscillatory nature. Lately, rhythmic oscillations in the electrical potential were observed at aqueous-organic interfaces [1–3]. The difference between dynamic and equilibrium behavior of the interface gives rise to local variation of the interfacial tension. This periodic agitation is termed as the Marangoni instability [4,5].

Yoshikawa et al. [6–12] first studied the chemically driven Marangoni instability on oil–water interface by taking an oil layer containing picric acid imposed between two aqueous phases in a U-tube. Recent studies used a cylindrical tube containing both nitrobenzene and an aqueous solution having a surfactant. Various surfactant molecules such as cetyl trimethylammonium bromide (CTAB) [2], sodium dodecyl sulfate [8], phosphatidyl ethanolamine (DPPE) [13] and sodium oleate [7,14] have been investigated. Several researchers studied the Marangoni instability with different liquids, surfactants and inorganic ions [15], and found contrasting results [6–12,16]. This could be attributed to the poor repeatability of the oscillations and their high dependability on specific procedures and setups. In most cases, the oscillations continued for 1–2 h before slowly fading away.

Dupeyrat and Nakache [1] proposed involvement of ion pair complexes between cetyl trimethylammonium (CTA^+) and picrate (P^-) ions to explain the interfacial movement. Another mechanism proposed by Yoshikawa et al. [9] involved a three-step process in which, first CTA^+ move towards the interface and position themselves with their hydrophilic heads towards the aqueous phase and hydrophobic tails in the organic phase. Simultaneously, the picrate ions move towards the interface increasing their concentration. In the second step, the concentrations of CTA^+ and P^- increase gradually and a monolayer structure forms at the interface. In the third and final step, when a critical mass is reached, the monolayer ruptures under its own weight and CTA^+ falls into the organic phase. Once the CTA^+ concentration at the interface decreases to a lower value, the system reverts back to the first step and repeats the whole mechanism until the critical CTA^+ concentration can no longer be reached. This mechanism also explains why no oscillations are observed in the presence of continuous stirring.

Considering the above mechanism, it can be argued that an entity that interacts with the monolayer and actively participates in the mass accumulation at the interface will affect the monolayer formation and thereby change the

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potential oscillations. Keeping this as the basis, we used gold-citrate nanoparticles with surfactant CTAB and studied the nature of the potential oscillations. As expected, considerable changes were observed in the measured parameters. Though clear evidence in the change in frequency is observed in presence of nanoparticles, the assumed model may not be sufficient to explain all the observed changes in the oscillation phenomenon and the effect of nanoparticles on it. The present investigations constitute an extension of our work on monolayer protected metal nanoparticles [16].

2. Experimental setup

Experiments were performed using the setup shown in Fig. 1. Very poor repeatability and high dependability of the oscillations on the experimental conditions made the procedure followed extremely critical. In our experiment, 7.5 ml of the organic solution of nitrobenzene and picric acid (1 mM) was taken in a beaker and a 2 cm diameter tube was inserted in such a way that 5 mm of it dipped into the solution. Srividhya et al. [17] and Yoshihisa et al. [18] found that a notch was necessary on the circumference of the dipped end of this tube for getting oscillations. Next, 15 ml of 0.1 M glucose was slowly added to the beaker on the outer side of the tube. Inside the tube, 2.5 ml of 9 mM CTAB was carefully added with a micropipette. The whole system was kept at room temperature (27 °C). The cell was completed by introduction of salt bridges (3 g agar–agar in 3 M KCl) and Ag/Ag^+ electrodes as shown in the figure. For a clearer observation of the oscillations, only 2 ml of CTAB was added initially. A careful addition of the remaining CTAB solution was done after the cell was complete. The voltage oscillations were recorded on an X–Y plotter and the data were acquired with a Keithley 2700 data acquisition system.

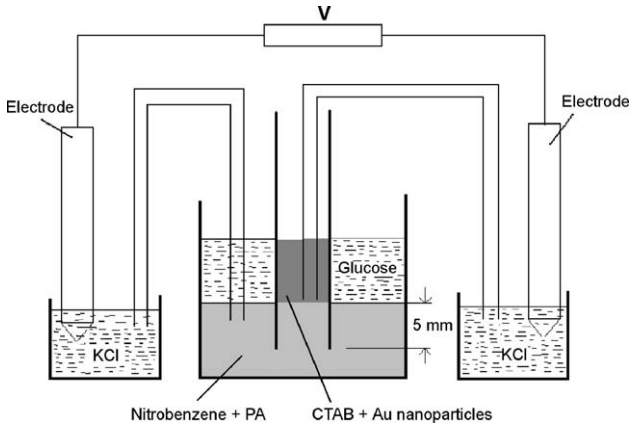

Fig. 1. Schematic of the experimental setup used for studying potential oscillations. 5 mm of the 2 cm diameter tube is dipped into the organic solution and the dipped end of the tube is given a notch of 1 mm. The cell is completed using two salt bridges and Ag/Ag^+ electrodes. The monolayer is formed at the CTAB–nitrobenzene interface.

The experiments were conducted with gold nanoparticles prepared by the citrate reduction route [19]. Briefly, the synthesis involves the following materials and methods: 1 ml of 0.005 M stock solution of $HAuCl_4 \cdot 3\ H_2O$ in water is diluted to 19 ml and heated until it begins to boil; 1 ml of 0.5% sodium citrate solution was added and heating continued till the color became pink. This solution was allowed to cool under continuous stirring. Transmission electron microscopy (TEM) was done with a Philips CM12 instrument. We used carbon coated copper grids to support the particles. Routine characterization of the particles was done with UV visible spectroscopy (Perkin Elmer Lambda 25).

3. Results and discussion

Fig. 2 shows the change in the nature of oscillations when a nanoparticle solution (0.05 ml solution as prepared above) was added. At a larger concentration of 9 mM CTAB, we get three oscillations within a time window of 400 s. This solution, when mixed with a solution of 10–15 nm Au-citrate particles (a TEM image of the particles is shown in the inset of Fig. 2b), gave a more uniform and delayed oscillation, as shown in Fig. 2b. Such an observation is very interesting since it shows that the Au nanoparticles are participating in the monolayer assembly at the interface. By considering the oscillation mechanism discussed above and by studying the effect of the nanoparticle constituents on the oscillations, it is possible to verify this conjecture.

The oscillatory model suggested by Yoshikawa et al. [9] is shown in Fig. 3a. The accumulation of the surfactant (CTA^+) and picrate (P^-) ions at the interface leads to a critical mass value and the layer falls under its own weight. Fig. 3b is an extension of the same model in presence of Au-citrate nanoparticles.

CTAB and the nanoparticles interact resulting in ligand substitution [20] and partially (or fully) monolayer functionalized nanoparticles are formed. These nanoparticles also assemble at the interface in addition to the free CTAB molecules, depending on the availability of the species. However, the assembly of nanoparticles containing CTAB is expected to be slower in comparison to the parent molecules. This is evident in Fig. 2, where the time delay for the potential build-up is shown to be significantly longer than that of the free molecule (see the insets of Fig. 2a and b). For CTAB solution, the time required for the potential to attain the maximum value after drop is 12 s, while for the nanoparticle added CTAB solution, it is 30 s.

To prove the fact that the variation in oscillations is due to the presence of gold nanoparticles and not due to the free citrate ions present in the nanoparticle solution, different concentrations of trisodium citrate solutions were mixed with CTAB and the oscillations generated were studied. It

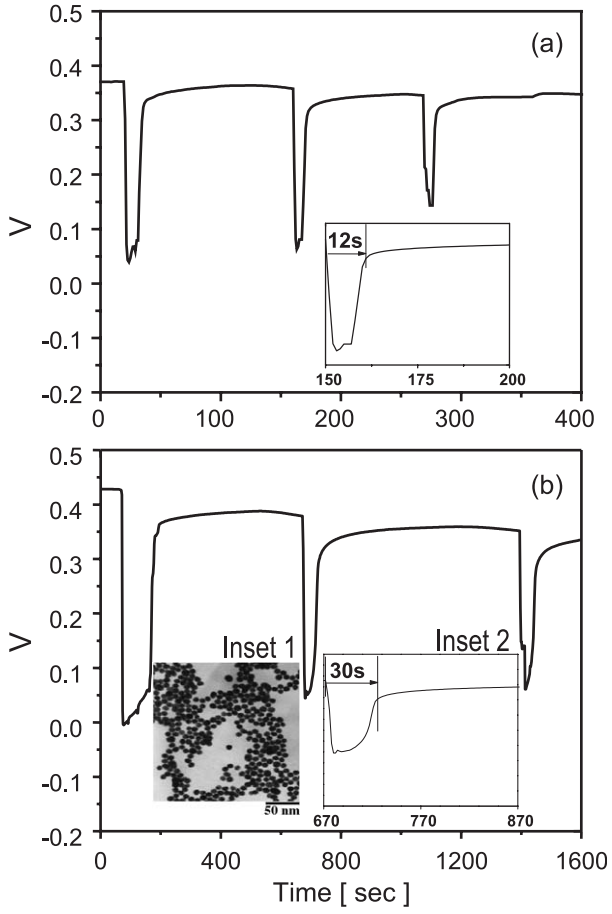

Fig. 2. Effect of Au-citrate nanoparticles on the oscillations: (a) shows the oscillations with no nanoparticles while (b) shows oscillations in the presence of Au-citrate nanoparticles. Note that the time scales for the abscissa are different for the two graphs. The oscillation frequency decreased on introduction of nanoparticles giving a clear indication of stabilization of the monolayer. No large change in the potential is observed in the two cases indicating a molecule-like behavior of the nanoparticles. The inset pictures compare the time of rise of potential to the maximum value after drop. The rise time is 30 s in case of nanoparticle-assisted oscillations while it is 12 s with CTAB solution alone. Inset 1 of (b) shows a TEM image of the gold nanoparticles used. The scale bar for TEM corresponds to 50 nm.

was observed that the oscillations were similar to the one observed with CTAB alone, suggesting the monolayer stabilization is due to gold nanoparticles.

To study the effect of Au-citrate nanoparticle concentration on the nature of oscillations and the stability of the monolayer, 3 ml of CTAB was taken and different amounts of nanoparticle solution (0.05, 0.1 and 0.2 ml) were added to it. This CTAB solution with the nanoparticles was stirred and allowed to mix for 5 min before addition to the setup. From the study of Fig. 4, it can be observed that the increase in the concentration of the nanoparticles increases the oscillation frequency. Although the role of Au-citrate nanoparticles on the critical micelle concentration was not studied, a clear evidence of the change in the monolayer dynamics is observed. The oscillation frequency variation can be attributed to the fact that more and more gold nanoparticles participate in the monolayer thus reaching the critical mass faster. Note that as the concentration becomes very high (in case of 0.2 ml of nanoparticle solution, Fig. 4c), the mass accumulation is faster and thus rapid oscillations.

The effect of particle size was also investigated. At very small particle sizes, the presence of the nanoparticles does not affect the interfacial phenomenon much except the fact that the oscillations will be observed for a longer period. This can be clearly seen in Fig. 5a. This is in contradiction with our general observation that a 9 mM CTAB solution without any clusters gives only a few oscillations highly squeezed in a narrow time span. The observation of oscillations for longer periods can be confirmed by the fact that the monolayer is now rich with gold nanoparticles which reduces the critical amount of CTAB required for oscillations to continue. Bigger particle sizes will help the monolayer achieve the required critical mass in a very small time giving an increased oscillation frequency.

In presence of nanoparticles, two opposing forces govern the oscillation frequency; the mobility of the particles assembling the monolayer and their mass. A high frequency will be observed with small and highly mobile particles as well as with large slow moving particles. Such an observation can be explained by the fact that monolayer rupture occurs when a critical mass at the interface is reached. This can happen in two ways. Small particles will produce the critical mass quickly by virtue of their high mobility. The

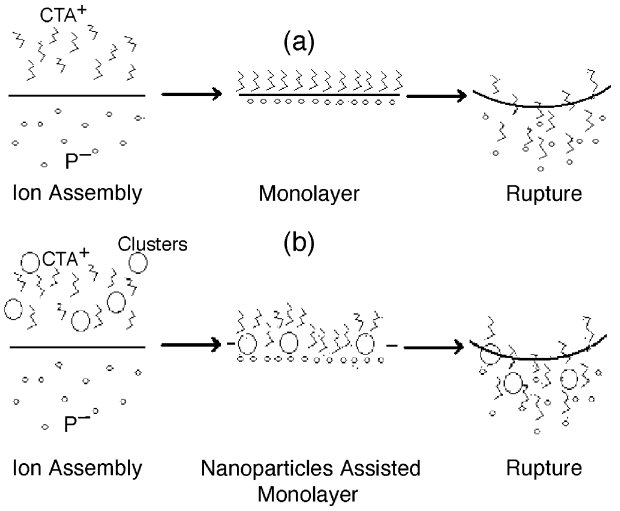

Fig. 3. (a) The monolayer formation and rupture model as suggested by Yoshikawa et al. [9]. The surfactant (shown as zigzag chains) binds with the picrate ions (shown as small circles) at the interface forming a monolayer, which ruptures under its own weight as the critical mass value is reached. (b) The modified model in presence of the Au-citrate nanoparticles (shown as large circles) showing the participation of the nanoparticles at the monolayer assembly. Nanoparticles mediated assembly and the assembly of free surfactants are suggested to occur.

same can happen with large, slow moving, particles since a small number of particles will be enough to increase the mass above the critical limit at the interface. Fig. 5 shows how the frequency increases with very small and very large particles in comparison with medium sized particles (whose oscillations are shown in Fig. 4a).

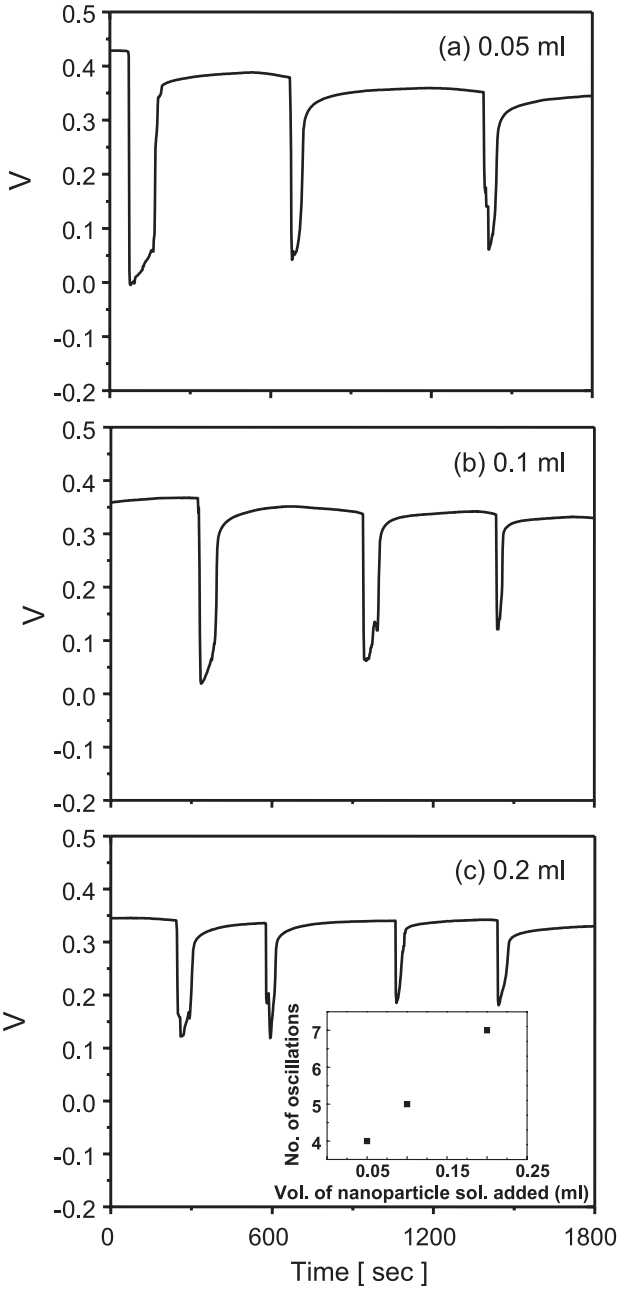

Fig. 4. The effect of nanoparticle concentration on the oscillations. 3 ml of 9 mM CTAB solution was added to increasing amounts of Au-citrate nanoparticles: (a) 0.05 ml, (b) 0.1 ml, (c) 0.2 ml; 2.5 ml of this solution was added to the setup for studying the effect of concentration on potential oscillations. As the concentration increases, the oscillation frequency increases showing that more and more nanoparticles are now participating in the monolayer formation allowing a rapid critical mass accumulation at the interface. Inset of (c) gives a variation of number of oscillations observed in the first 3000 s versus the volume of nanoparticle solution added. Exact concentration was not determined, but is linearly related to the volume added.

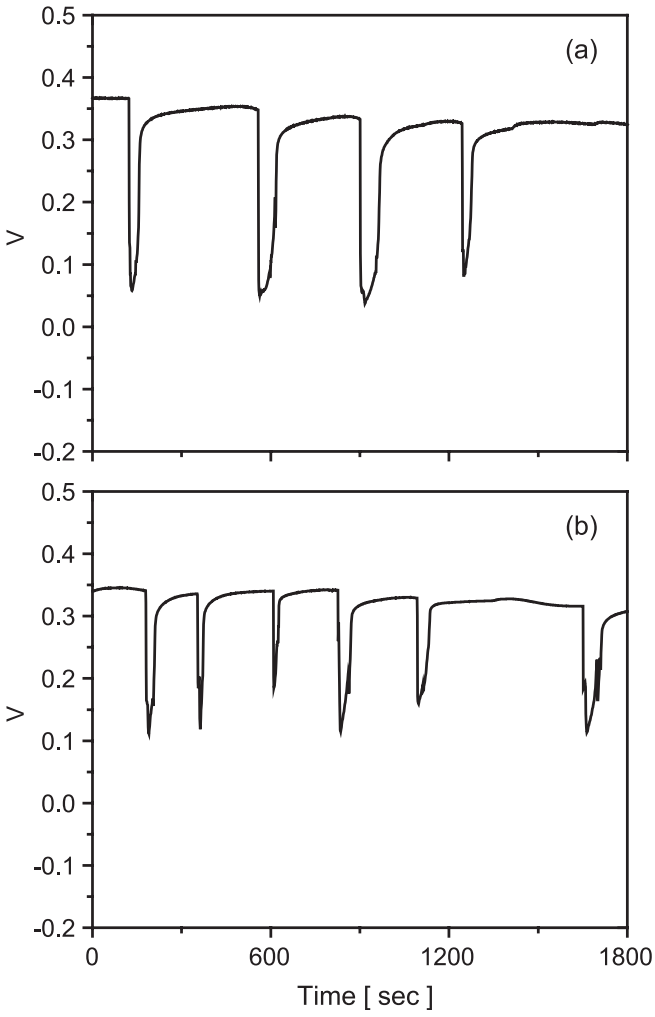

Fig. 5. Variation in oscillations as a function of particle size. The oscillations shown are for two different particle sizes, (a) 5–7 nm and (b) 25–30 nm. Note that the frequency has increased in both the cases compared to 10–15 nm gold particles that were used in all the other experiments (Figs. 2 and 4). Higher frequency of oscillations can be obtained by virtue of mobility of small particles or by the higher mass of bigger particles, both allowing a faster accumulation of the critical mass at the interface.

4. Conclusion

From the observations made, it can be concluded that the presence of gold nanoparticles help in the stabilization of the monolayer at the organic-aqueous interface. The presence of gold nanoparticles in the monolayer is reflected in the build-up time of the potential. Increase in nanoparticle concentration increases the frequency of oscillations. The same behavior is observed with increase in particle size. A mechanism to explain this phenomenon is suggested based on the previous reports and present observations. The data

suggest that oscillations of interface potential can be used to investigate nanoparticle induced assemblies.

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