

Surface activity and collective behaviour of colloidally stable Janus-like particles at the air–water interface

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M. A. Fernández-Rodríguez, M. A. Rodríguez-Valverde, M. Cabrerizo-Vílchez and R. Hidalgo-Alvarez*

In this work we report an experimental study on the surface activity and the collective behaviour of colloidally stable Janus-like silver particles at the air–water interface. The colloidal stability of silver nanoparticles has been enhanced using different capping ligands. Two polymers coated the silver particles: 11-mercaptopundecanoic acid and 1-undecanethiol. These capping ligands adsorbed onto the particle surface are spontaneously rearranged at the air–water interface. This feature leads to Janus behaviour in the silver particles with amphiphilic character. The surface activity of the silver particles at the air–water interface has been measured using pendant drop tensiometry. The Janus-like silver particles revealed a surface activity similar to that shown by conventional amphiphilic molecules but with much larger area per particle. The variation of the surface pressure with the area per particle was described properly using the Frumkin isotherm up to the collapse state. Furthermore, oscillating pendant drop tensiometry provided very useful data on the rheological properties of Janus particle monolayers; these properties depended on the lateral interactions between particles and were closely related to the monolayer microstructure. We revealed the close relationship between the collective behavior and the surface activity of Janus-like silver particles.

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Introduction

Janus Particles (JPs) are special types of particles whose hemispheres have two or more distinct physical or chemical properties.¹ In recent years, there has been increasing interest in the design and synthesis of JPs and their self-assembly and physical properties are being further addressed.^{2–8} There are many reasons to think that JPs are a very interesting colloidal system for electronic paper, asymmetrical carriers for catalysis, sensing and drug delivery, nanoscale machinery in the conversion of solar energy into electrical current and colloidal surfactants.⁹ To develop these applications it is mandatory to evaluate properly the colloidal stability in bulk and the interfacial activity of JPs and their connection. However, there are a few studies devoted to study these properties. The first experiments on the interfacial activity of JPs (gold and an iron oxide moiety) at liquid–liquid interfaces (water–hexane) were reported by Glaser *et al.*, using pendant drop tensiometry.¹⁰ Most recently, Ruhland *et al.*¹¹ have performed the first study on the self-assembly behaviour of Janus cylinders at liquid–liquid interfaces using the pendant drop technique and microscopic imaging. Kumar *et al.*⁸ have published a review on amphiphilic JPs at fluid interfaces where they survey the recent development in the use

of these particles as colloidal surfactants to stabilize multiphase mixtures such as emulsions. They also discuss on the importance of controlling the shape of JPs, which has a significant impact on their behaviour at fluid interfaces. Obviously, the area of JPs occupied at the interface changes drastically as they aggregate because they lose their original size and shape.

The surface characterization of colloidal monolayers formed by JPs becomes a difficult task.^{12,13} To explore the surface activity of spherical JPs at fluid interfaces, the following factors are crucial: the colloidal stability of the particles in bulk, the presence of traces of the surface-active reagents used in the particle synthesis and of the spreading agent employed to prepare the colloidal monolayer. These factors hinder the effect of the interface area on the surface pressure due exclusively to the presence of amphiphilic particles. Park *et al.*¹⁴ have studied the self-assembly behaviour of JPs at fluid interfaces in detail. These authors found that JPs form a fractal-like aggregate structure spontaneously, which means that their interactions are predominantly attractive. The formation of aggregates at fluid interfaces makes unrealizable the study of colloidal monolayers, because these aggregates lead to multilayers or unresolved monolayers. Instead, as reported by Luo *et al.*,¹⁵ a stable colloidal monolayer can be formed with electrically charged JPs. Simulations performed by Hong *et al.*¹⁶ on the assembly of charged Janus spheres showed that the charge asymmetry of individual JPs is preserved in the cluster acting as a larger charged JP.

Biocolloid and Fluid Physics Group, Applied Physics Department, Faculty of Science, University of Granada, E-18071 Granada, Spain. E-mail: rhidalgo@ugr.es

The extremely low colloidal stability of JPs is a serious limitation in their utilization as colloidal surfactants. From theoretical calculations, an amphiphilic particle, half hydrophobic and half hydrophilic, can be up to three times more surface active than the corresponding homogeneous particle.¹⁷ In these energetic calculations, the JPs are not coagulated, which is rather difficult to achieve experimentally if the particles exhibit a strong wettability contrast between both hemispheres. To avoid the coagulation of the JPs we have prepared silver particles coated by a mixture of hydrophobic and hydrophilic ligands in appropriate proportions, which go through a phase separation when the particles are located at the air–water interface. Very recently, Sashuk *et al.*¹² have experimentally confirmed the Janus behaviour of this type of particle. The electrical charges of the hydrophilic ligand play a decisive role in the stabilization of silver particles and the long alkyl chain of the hydrophobic ligand also introduces a steric effect between particles. A combination of both effects is expected to stabilize silver particles through an electrosteric mechanism. As reported by Garbin *et al.*, capping ligands play a prominent role in determining both interparticle interactions and the particle–fluid interactions.¹³

In this work, we examined the surface activity and the collective behaviour of colloiddally stable silver Janus-like particles (AgJPs) deposited at the air–water interface. First, using pendant drop tensiometry, we measured the surface tension of JP monolayers as a function of time at different particle surface concentrations and the corresponding adsorption isotherms (surface pressure as a function of area per particle). Next, the rheological response of these colloidal monolayers was evaluated using oscillating pendant drop tensiometry. An attempt has been made to relate the rheological properties of JP monolayers to the lateral interactions between particles and the monolayer microstructure.

Experimental

Preparation of negative Janus-like Ag particles (AgJPs)

Silver nanoparticles (AgNPs) were prepared using the procedure described by Jana and Peng.¹⁸ Firstly, 344 mg of decanoic acid (DA) were dissolved into 20 mL of toluene. Next, 6.4 μ L of anhydrous N_2H_4 were dissolved into DA solution by sonication. This solution was then mixed with 0.2 mL of dilute *tert*-butyl ammonium bromide (TBAB) solution (5.0 mg of TBAB in 20 mL of toluene). Finally, 34 mg of silver acetate dissolved in 0.4 mL of dodecyl amine solution (1 M) in toluene were injected during stirring. Dark red colour appears within 5 minutes of mixing indicating particle formation. Stirring continued for 10–15 minutes until the reaction was completed. Next, Janus-like silver particles (AgJPs) were prepared using the procedure described by Sashuk *et al.*,¹² with certain modifications. Firstly, 20 mL of methanol were added to a solution of DA-capped AgNPs (0.02 mmol Ag, 2 mL). After precipitation of nanoparticles, the supernatant solution was decanted. The resulting nanoparticles were dissolved in 5 mL of chloroform. Nanoparticle solution was injected into a solution of 11-mercaptopundecanoic acid and 1-undecanthiol ligands (0.04 mmol) of a

given ratio (1 : 1) in dichloromethane (5 mL) upon stirring. The reaction mixture was stirred overnight. Then the nanoparticles were centrifuged and purified by dissolution–precipitation. The nanoparticle precipitate was dissolved in methanol (1.5 mL) followed by the addition of 1.5 mL of 2-propanol and precipitated with *n*-cyclohexane (40–50 mL). Precipitated AgJPs were centrifuged (5000 rpm) and the dissolution–precipitation cycle was repeated twice. Finally, 2 mmol of AgJPs were dissolved in 3 mL solvent (1.5 mL 2-propanol and 1.5 mL methanol). From Scanning Electron Microscopy (SEM), an average particle diameter of (100 ± 40) nm was obtained by particle size distribution (see Fig. 1).

Using photon correlation spectroscopy (Malvern 4700c Dynamic Light Scattering) we monitored the time dependence of the average diameter in a 10^{-2} M KBr solution and it remained practically constant during almost one and a half hour. Longer times were not possible to be measured due to particle sedimentation. This proved that the AgJPs were stable in the colloidal sense. Sashuk *et al.*¹² demonstrated the Janus behaviour of this type of silver particle at the air–water interface, although they indeed do not behave as JPs in bulk solution. The average size of our AgJPs is much larger than the nanoparticles prepared by Sashuk *et al.* (~ 5 nm).¹² Fresh Milli-Q water was used for the preparation of aqueous solutions. All glassware was washed with 10% Micro-90 cleaning solution and exhaustively rinsed with water, isopropanol, deionized water, and Milli-Q water in this sequence. All chemicals (Aldrich and Panreac) were of analytical grade and used as received.

Experimental methods

The electrophoretic mobility of the AgJPs was measured with a Nano Zeta-Sizer (Malvern) at room temperature. Pendant drop tensiometry is an extensively employed method for measuring the surface and interfacial tension of liquids.¹⁹

The surface tension of AgJPs was measured using pendant drop tensiometry. This technique enables us to measure the surface or interfacial tension of colloidal monolayers using a much smaller amount of particles than that used in the conventional technique of the Langmuir balance, where the

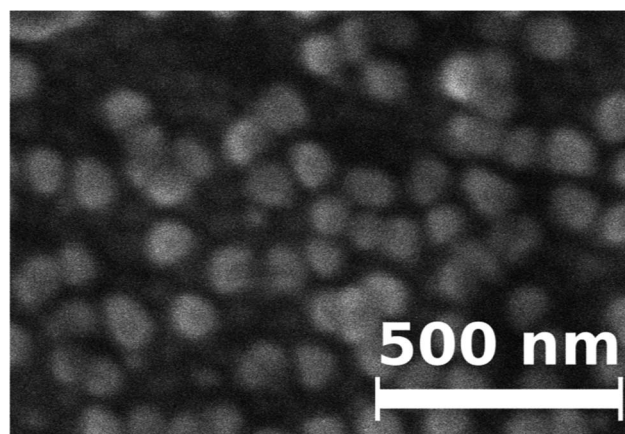


Fig. 1 SEM micrograph of the AgJPs studied.

particles are spread on a fluid subphase from a volatile solvent to form the monolayer.¹³ Instead, the colloidal monolayer is formed onto the surface of a 20 μL pendant drop depositing a given amount of solution with nanoparticles (see Fig. 2).

This is very important because simple strategies are still being developed for the preparation of large amounts of JPs.⁴ Our set-up is composed of a CMOS camera interfaced with a computer-based data acquisition system, which is used to capture the image of an equilibrium drop.²⁰ Then edge-detecting software is used to fit the drop shape to the Young–Laplace equation using the Axisymmetric Drop Shape Analysis Profile (ADSA-P).¹⁹ In our case, increasing and decreasing the volume of a Milli-Q water pendant drop with AgJPs deposited carefully at the air–water interface allowed exploration of the dynamic surface response of the monolayer. Real time drop images were processed at each step of volume variation and the drop area and surface tension were calculated (see Fig. 3).²⁰

The dilatational rheology of the colloidal monolayers formed at the air–water interface from different surface particle concentrations was measured using oscillating pendant drop

tensiometry. A periodic variation in the volume of the drop was produced by the injection and extraction of liquid to and from the drop, sequentially. The system monitors the response of the surface tension to the drop area deformation. The dilatational modulus (E), the mean surface tension (γ) and the surface dilatational viscosity (η_d) were obtained from this response. This experimental procedure requires a quasi-equilibrium drop shape for the calculation of surface tension. Hence, the oscillations applied to the drop area were maintained below 1% of amplitude to avoid excessive perturbations of the colloidal monolayer and the departure from the viscoelastic linear region. The initial pendant drop volume was 20 μL or 10 μL , which depended on the surface particle concentration. In all rheology experiments, we applied a sinusoidal oscillation in the pendant drop volume with 1 μL amplitude and a frequency of 0.1 Hz.

Results and discussion

The electric state of the AgJPs in aqueous media was analysed by measuring the electrophoretic mobility as a function of pH at a constant ionic strength of 10^{-2} M of KBr. As can be seen in Fig. 4, the electrophoretic mobility of AgJPs is negative and pH-dependent. The ζ -potential of AgJPs obtained using the Smoluchowski equation varies from $-(8 \pm 6)$ mV (3.3 pH) to $-(46 \pm 11)$ mV (10.8 pH). According to these ζ -potential values, the AgJPs were colloidally stable at pH values above 5. All experiments of surface activity and collective behaviour were performed at pH ~ 6 .

To explore different interfacial coverage degrees of AgJPs, the surface activity experiments were performed with different amounts of particles deposited at the surface of a Milli-Q water pendant drop. Each experiment involved two stages:

(1) Deposition of a certain amount of AgJPs suspended in a spreading agent onto the surface of a 5 μL drop in air using a 5 μL microsyringe (Hamilton) and a micropositioner. As can be seen in Fig. 2, while the spreading solvent evaporates, the drop volume slowly increased at $0.08 \mu\text{L s}^{-1}$ up to 10 μL (the first

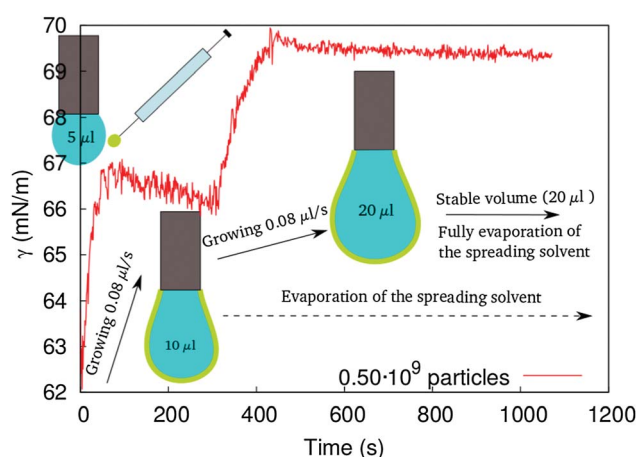


Fig. 2 Temporal evolution of surface tension at the air–water interface with 0.50×10^9 particles deposited over a droplet of 5 μL .

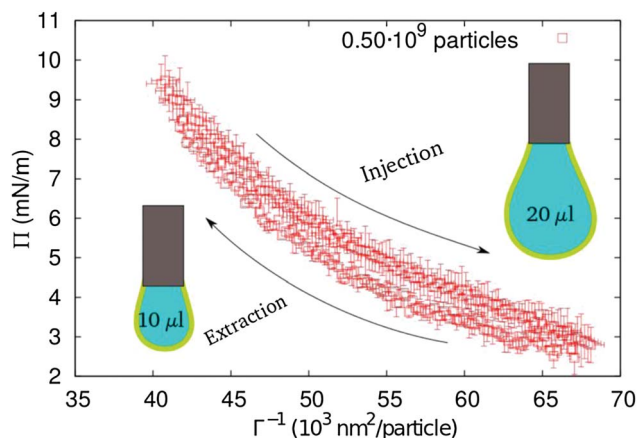


Fig. 3 Hysteresis cycle of the growing and shrinking of the pendant droplet with 0.50×10^9 particles.

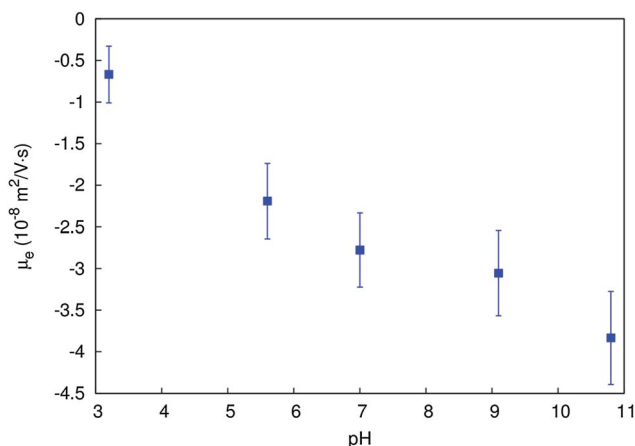


Fig. 4 Electrophoretic mobility of the AgJPs as a function of pH at 2×10^{11} particles per mL and 10^{-2} M KBr.

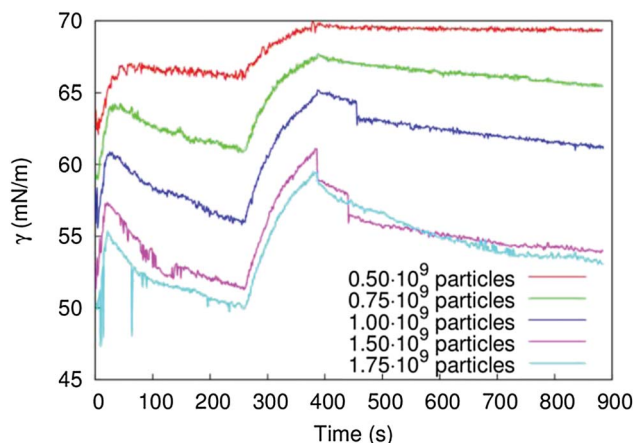


Fig. 5 Surface tension as a function of time during the formation of a pendant drop just after the deposition of the AgJPs, at different particle concentrations. The first increase observed in the surface tension was produced by the spreading agent evaporation and the second increase at 250 s was produced by the drop growing.

increase of surface tension observed in Fig. 5). Next, the drop volume was maintained constant for 3 minutes. Then, the drop volume was increased up to 20 μL (the second increase of surface tension) and maintained until the surface tension stabilized. This stage of the pendant drop experiment finished once the spreading solvent was fully evaporated.

(2) Shrinking and growing of the air–water interface at $0.08 \mu\text{L s}^{-1}$ within a volume range from 20 μL to 10 μL . The shrinking of the pendant drop was repeated three times and the growing twice. The shrinking and growing stages were accordingly averaged for each particle concentration.

After the first stage of the pendant drop experiments, the final surface tension decreased as increasing amounts of AgJPs were deposited at the interface. As can be seen in Fig. 5, the final surface tension decreased by 15 mN m^{-1} when the amount of AgJPs deposited was increased 3.5 times. Furthermore, a decreasing trend in the surface tension with time was observed particularly as the particle concentration increases. As is well known, getting completely stationary values of surface tension when particles are adsorbed at fluid interfaces is a very difficult task to accomplish. In our case the maximum rate of variation of the surface tension with time is around $10^{-3} \text{ mN m}^{-1} \text{ s}^{-1}$. In any case this variation of the surface tension is within the experimental fluctuations of our measurements.

To examine the effect of the spreading agent on the surface tension of the AgJP monolayers, we used two different volatile liquids (methanol and 1 : 1 methanol–propanol). Two pendant drops were formed with the supernatants obtained from the solutions with 10^9 particles dispersed in methanol and the methanol–propanol mixture (centrifugation at 14 000 rpm for 15 minutes). The methanol–propanol mixture as the spreading agent was not fully evaporated compared to methanol for 2–3 minutes because the surface tension reached values lower with methanol–propanol than with methanol (see Fig. 6).²¹

For each shrinking and growing experiment, the surface pressure $\Pi = \gamma_0 - \gamma$, where γ_0 is the surface tension of water

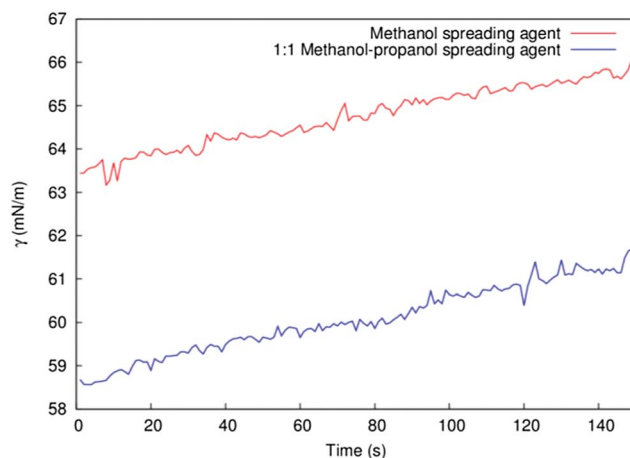


Fig. 6 Surface tension as a function of time for the supernatants extracted from methanol and 1 : 1 methanol–propanol solutions of AgJPs. The increase observed is due to the drop evaporation.

and γ is the measured surface tension of the colloidal monolayer, against the drop area divided by the number of AgJPs was plotted. The effective surface tension γ of a JP-laden interface is lower than the surface tension γ_0 of the bare interface due to the bidimensional osmotic pressure Π generated by the colloidal monolayer, $\gamma = \gamma_0 - \Pi$. In thermodynamic equilibrium, Π is a function of the surface density of JPs, Γ . To the best of our knowledge, there are no experimental data of $\Pi(\Gamma)$ for JP monolayers formed at the air–water interface.

In Fig. 7, the compression isotherm of the AgJPs dispersed in methanol–propanol is plotted. Near the collapse zone, the highest surface pressure measured is $\sim 45 \text{ mN m}^{-1}$. This value of surface pressure is higher than that obtained in previous studies using similar AgJPs, which is attributable to the spreading solvent effect, not fully evaporated because of the

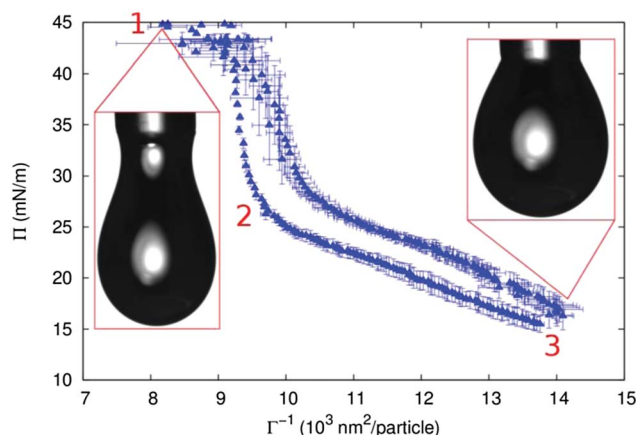


Fig. 7 Surface pressure as a function of surface area per particle for 2.5×10^9 AgJPs using 1 : 1 methanol–propanol solution as the spreading agent. This experiment was conducted with several growing/shrinking cycles but at a fixed amount of AgJPs. Inset: drop pictures under the most compressed and expanded states. Inset numbers indicate the compression states of the colloidal monolayer used in the rheology experiments (see Table 1).

stable molecular aggregates formed between propanol and water.²¹ However, the hysteresis displayed by the isotherm in Fig. 7 is much smaller than that shown by the isotherms obtained by the conventional Langmuir balance.¹² This indicates that pendant drop tensiometry enables us to measure surface pressure values under experimental conditions very close to the thermodynamic equilibrium and that the migration of AgJPs deposited at the interface into the aqueous phase is almost negligible. In the case of high surface pressure (*i.e.* low surface tension), the pendant drop was highly deformed (see the inset in Fig. 7). Under these conditions, the pendant drop also exhibited higher surface elasticity as the rheology results (see Table 1).

We performed shrinking and growing experiments for different amounts of AgJPs deposited at the air–water interface. Since the values of drop volume and area were fixed in all experiments, the drop area divided by the number of AgJPs deposited at the interface enabled us to reproduce a piecewise compression isotherm rather than a traditional compression isotherm, such as that obtained with the Langmuir balance.¹² This is noticeable in Fig. 8 using methanol as the spreading

agent. The number of particles was enough to form a monolayer for all concentrations and compression states above 1.0×10^9 particles.

We observe in Fig. 8 how the low hysteresis found in the isotherms is further lower due to the surface tension error. The interface compression produced changes in the surface pressure ($\sim 5 \text{ mN m}^{-1}$) at high values of area ($5 \times 10^4 \text{ nm}^2$ per particle), which reveals the sensitivity of this technique. Below this point a gas–liquid transition can be identified from the steep rise in the surface pressure. It is noticeable that the complete compression isotherm throughout the range of interfacial area is not single-valued, *i.e.* the curves obtained with different particle concentrations do not overlap perfectly. This can be explained because each part of the compression isotherm corresponds to a different shrinking and growing experiment with different AgJP amounts in which different self-assembly dynamics could take place. The isotherm collapse is found in Fig. 8 between 10^4 and $2 \times 10^4 \text{ nm}^2$ per particle. This collapse might correspond to the close packing of 100 nm particles at the interface, which takes place when the area per particle is $4R^2$, R being the particle radius (a hexagonally close-packed monolayer). Moreover, the surface tension at the collapse state ($\sim 25 \text{ mN m}^{-1}$) is in agreement with the reported values for similar AgJPs.¹² The contact angles of both hemispheres of the AgJPs are expected to be around 80° and 92° , which do not represent a large wettability contrast in both faces of the AgJPs used in this study.¹² This reveals that the colloidal stability of the AgJPs in the bulk solution and at the interface plays a more important role in their interfacial activity rather than the contact angle difference between their faces.

The Frumkin equation for a monolayer relates the surface pressure (Π) with the area per particle at the interface (Γ^{-1}) as follows:²³

$$\Pi(\Gamma) = -\frac{k_B T}{a} \ln(1 - a\Gamma) - \beta \Gamma^2$$

where k_B is the Boltzmann constant, T is the temperature, a is the particle geometrical area and β is the interaction constant. The Frumkin equation was fitted to the experimental data in Fig. 8 before the collapse, resulting in the dashed black line. The first term of the equation is referred to the geometry of the system (*i.e.* how the particles are arranged at the interface) and the second term describes the interaction between the particles at the interface. The first term is negligible for our experimental data but the second term is fitted with a positive value of $\beta = (1.15 \pm 0.08) \times 10^{-26} \text{ mJ m}^2$. The negligible geometrical term in comparison with the high interaction term points out to the dominant effect of the lateral attractive interactions between AgJPs at the air–water interface.

The dilatational rheology of the colloidal monolayers at the air–water interface has been studied using the procedure described in the experimental methods with different AgJP concentrations and under different values of surface pressure and compression states. This has allowed us to explore the collective behaviour of the AgJP particles at the interface. Table 1 shows the values obtained for the dilatational modulus (E) of the colloidal monolayer, the mean surface tension (γ) and

Table 1 Dilatational rheology response of the AgJP monolayer under different compression states. States 1, 2 and 3 correspond to the values obtained with three different compression states on the isotherm shown in Fig. 7, whereas states 4 and 5 refer to two compression states of the isotherm shown in Fig. 8

Compression state of the AgJP monolayer	E (mN m^{-1})	η_d (mN ms^{-1})	γ (mN m^{-1})
1	620 ± 50	14.0 ± 0.1	34 ± 1
2	69 ± 2	3.3 ± 0.2	48 ± 1
3	62 ± 2	2.2 ± 0.2	57 ± 1
4	23 ± 1	1.71 ± 0.05	47 ± 1
5	28 ± 2	1.0 ± 0.1	65 ± 1

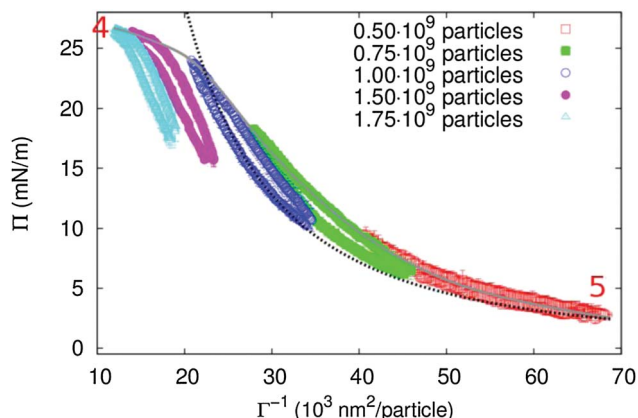


Fig. 8 Surface pressure as a function of surface area per particle for different particle concentrations using methanol as the spreading agent. The dashed line corresponds to the Frumkin model fitting and the solid line serves as a guide to the eye. Inset numbers indicate the compression states of the colloidal monolayer used in the rheology experiments (see Table 1).

the surface dilatational viscosity (η_d).²² We can distinguish two different behaviours depending on the spreading agents used for the deposition of the AgJPs. The results, corresponding to the states 1, 2 and 3 obtained from the compression isotherm performed with the methanol–propanol mixture (Fig. 7), indicate that the dilatational modulus changed dramatically when the colloidal monolayer collapsed (state 1), whereas the dilatational modulus remains practically constant when the AgJPs adopted a close-packed hexagonal structure (states 2 and 3). A similar behaviour was observed for the values of surface dilatational viscosity obtained with the three compression states. The states 4 and 5, reproduced from the isotherm performed with methanol as the spreading agent (Fig. 8), corresponded to the collapsed and extended colloidal monolayer, respectively. The values of both E and η_d obtained upon these compression states agree, which indicates that the collective behaviour of the AgJPs is practically independent of the arrangement of particles in the colloidal monolayer. This illustrates again the decisive role played by the spreading agent. The collapsed monolayer was reproduced to lower values of surface pressure using methanol ($\sim 25 \text{ mN m}^{-1}$) instead of the mixture of methanol–propanol ($\sim 45 \text{ mN m}^{-1}$). The elastic network formed by the AgJPs at the interface at high surface pressure is strongly influenced by the presence of solvent molecular clusters established with water.²¹

Conclusions

The surface activity of colloidally stable Janus-like silver particles at the air–water interface was experimentally determined using pendant drop tensiometry. These particles revealed a surface activity similar to that shown by amphiphilic molecules but with much larger area per particle. We have demonstrated the interplay between bulk colloidal stability and surface activity of Janus-like particles. Oscillating pendant drop tensiometry provided very useful data on the rheological properties of the Janus-like silver particle monolayers; these properties depended on the lateral interactions between particles and were closely related to the monolayer microstructure.

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