

Surface Tension of Charge-Stabilized Colloidal Suspensions at the Water–Air Interface

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In this paper, we show that the surface tension of charge-stabilized titania suspensions strongly depends on the particle concentration. The surface tension first decreases significantly with an increase in the weight percent and then increases with a further increase in the weight percent. Thermodynamic arguments are used to explain the initial decrease in the surface tension for lower particle concentrations. For higher concentrations, it is hypothesized that the capillary forces acting between the immersed particles at the interface cause the increase in the surface tension.

Introduction

Suspensions or dispersions of particles in a liquid medium are ubiquitous. Control of the structure and flow properties is vital to the processing and properties of such suspensions. For example, during the coating of dispersions, the surface tension is often an important parameter that determines the film properties. Over the past few years, there has been an increasing interest in the behavior of solid particles at liquid surfaces in the absence of other surface-active materials such as surfactants or polymer molecules.

When the surface tension of a viscous fluid is not uniform, spatial gradients of the surface tension will create a surface shear that can only be balanced by shear flow in the adjacent surface layers. The general phenomenon is known as Marangoni flow, and the surface tension gradient driving the flow can be caused by temperature gradients (thermocapillary flows), surface concentration gradients (solutocapillary flow),¹ and electric charges (electrocapillary flows).^{2–4} Recently, Casson and Johnson have shown that simple colloidal particles can also create capillary flows.⁵ They demonstrated the capillary flow for a variety of particles: 5 and 50 μm polyamide particles and 5 μm silver-coated silica particles. In their paper, they hypothesized that the aggregates of colloidal particles at the interface create a localized decrease in the surface tension. These aggregates therefore generate surface tension gradients that cause significant capillary flows.

There have been several investigations of the adsorption of particles at the water–air or water–oil interface.^{6–8} Results show that the particles are strongly attached to the fluid (α)–fluid (β) interface, whether the particles are hydrophobic or hydrophilic. Consider a spherical particle of radius r that is initially in phase β and is

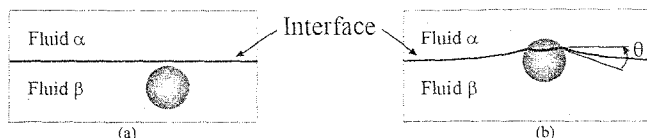


Figure 1. Schematic diagram before (a) and after (b) the adsorption of a spherical particle to the interface. After the adsorption of the particle at the interface, an area of the $\beta\beta$ interface is replaced by an equal area of the $\alpha\alpha$ interface. At the same time, an area of the $\alpha\beta$ interface is also lost.

subsequently adsorbed to the $\alpha\beta$ interface (Figure 1). The interfaces $\alpha\alpha$, $\beta\beta$, and $\alpha\beta$ have interfacial tensions $\gamma_{\alpha\alpha}$, $\gamma_{\beta\beta}$, and $\gamma_{\alpha\beta}$, respectively. Ignoring the line tension acting at the three-phase contact line ($\alpha\beta\beta$), adsorption of the particles at the interface results in an area $\beta\beta$ being lost but being replaced by an equal area of the $\alpha\alpha$ interface. More importantly, however, an area of the $\alpha\beta$ interface (normally of high tension) is also lost due to the presence of the particles, and this area depends on the contact angle, θ . Assuming the particle is small enough so that the effect of gravity is negligible, the energy E required to remove the particle from the interface to the α phase or β phase is given by

$$E = \pi r^2 \gamma_{\alpha\beta} (1 - \cos \theta)^2 \quad (1)$$

where θ is the contact angle based on the β phase.⁹

Paunov et al. investigated the adsorption of individual particles on a liquid–fluid interface and developed a thermodynamic approach to the adsorption of spherical charged colloidal particles on the water–air interface.¹⁰ They ignored the entropic contribution of the change on the free energy and derived the adsorption equation for the case when the air–water interface is not charged. Their results show that the total free energy favors the adsorption of the particles to the air–water interface and the formation of the double layer at the particle surface can make the particles more hydrophobic (a larger true contact angle θ). On the other hand, collective effects of charge accumulation or charge displacement can regulate or suppress the adsorption.

When particles are placed at an interface, they are typically classified into two categories: flotation or im-

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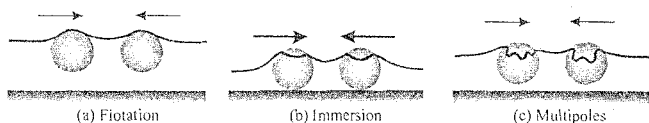


Figure 2. Schematic of two particles at an interface. (a) If the particles are freely floating at the interface, it is said to be "flotation" and the origin of the capillary force is the particle weight. (b) If the particle is partially confined into a liquid layer, it is considered "immersion" and the origin of the capillary force is the wetting of the particle by the liquid. (c) If the contact line on the particle surface is irregular (i.e., undulated), a multipole–multipole capillary force exists between the particles.

mersion, where the particles are freely floating at the interface or partially immersed (confined) into a liquid layer, respectively (Figure 2). For both conditions, lateral capillary forces are created by the deformation of the interface. For flotation forces, the particles are attracted by the hydrostatic pressure created by the interface deformation. This force is proportional to the radius to the sixth power and is therefore negligible for particles less than $10\ \mu\text{m}$.¹¹ However, for the immersed particles, the particle attraction is related to the wetting properties of the particle surface. The immersion force depends on the square of the particle radius and is significant for particles as small as a few nanometers.¹² The interaction energy between these two immersed particles is estimated by eq 2.

$$\Delta W = 2\pi\gamma_{\alpha\beta}Q^2K_0(qL) \quad (2)$$

where $\gamma_{\alpha\beta}$ is the surface tension, $Q = r \sin(\theta)$ is the capillary charge of the particle, r is the radius of the contact line, θ is the meniscus slope angle at the contact line, $q = \Delta\rho g / \gamma_{\alpha\beta}$, $\Delta\rho$ is the density difference between the two fluids, g is gravity, and K_0 is the modified Bessel's function of zero order. The interaction energy, ΔW , is appreciative (with respect to the Boltzmann energy) even for particles separated by several millimeters. The capillary interaction energy indicates that a random displacement of particles on an interface will eventually attract each other and form aggregates. This strong attractive force between particles will resist the deformation of the interface and change the effective local surface tension.

Furthermore, if the contact line on the particle surface is irregular or undulated (Figure 2c), a multipole–multipole interaction exists between floating particles. The leading multipole capillary force between two floating particles is the quadrupole–quadrupole interaction; the respective interaction energy is¹³

$$\Delta W = 12\pi\gamma_{\alpha\beta}h_c^2 \cos(2\varphi_A + 2\varphi_B) \frac{r_c^4}{L^4} \quad (3)$$

where h_c is the amplitude of the undulation of the contact line, whose average radius is r_c . The angles φ_A and φ_B are subtended between the diagonals of the respective quadrupoles and the line connecting the centers of the two particles. This multipole interaction is proportional to the fourth power of the radius and inversely proportional to the fourth power of the separation distance, L . Therefore, this interaction is significant only when the particles are close together. For two particles in contact ($L/r_c = 2$) and

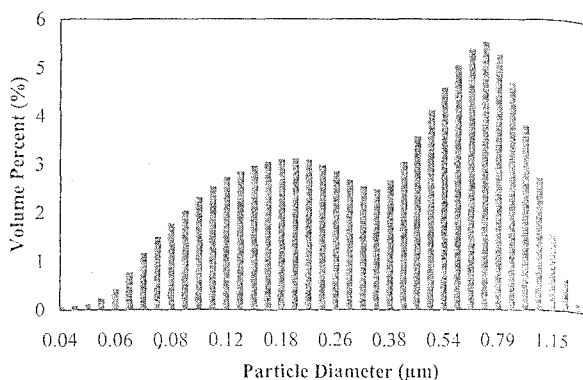


Figure 3. The histogram of the TiO_2 particle volume distribution. The particles were measured by the Beckman Coulter Particle Characterization Laboratory using a LS13 320 particle size analyzer.

optimal orientation, $\cos(2\varphi_A + 2\varphi_B) = 1$, one obtains $\Delta W = (3/4)\pi\gamma_{\alpha\beta}h_c^2$. Thus, for surface tension $\gamma_{\alpha\beta} = 72\ \text{mN/m}$, the interaction energy becomes greater than the thermal energy kT for undulation amplitude $h_c > 1.6\ \text{\AA}$. This result shows that even a minimal roughness of the contact line can give rise to a significant capillary attraction.

Okubo investigated the surface tension of dilute, monodisperse, nanometer-sized, colloidal dispersions of polystyrene and silica spheres at the water–air interface. Using 12 types of latex particles of different size and density, it is concluded that the surface activity is high only for surfaces that contain a crystal-like structure. In suspension. At a constant volume concentration (0.1), the surface tension passes through a sharp minimum for particle diameters of approximately 100 nm, the lowest being as much as 20 dyn/cm (from that of water at 72 dyn/cm). By contrast, the surface tension of aqueous suspensions of hydrophilic spherical silica particles shows less surface activity. For the interfacial colloidal structures that were either gas or liquidlike, the surface tension remained constant or increased slightly with concentration. For dispersions that displayed crystal-like structures in the bulk, the surface tension did decrease, but only as much as 2 dyn/cm.

In the remainder of this paper, we will report our recent experimental results on the surface tension measurements of concentrated, charge-stabilized titania (TiO_2) dispersions. We will show that the concentrations of these dispersions have a significant effect on the surface tension. The surface tension first decreases with the increase of the concentration and passes through a minimum for particle weight concentrations of approximately 10%. Further increases in the concentration increase the surface tension. When the concentration of the dispersion is at 10%, the surface tension actually increases to a value slightly larger than the surface tension of pure water. This is in comparison to Okubo's results for hydrophilic silica particles where very little change in the surface tension was witnessed.

Materials and Procedure

Dispersion Materials and Preparation. The TiO_2 particles were purchased from DuPont Chemical Co., the particle size distribution (Figure 3) is from 0.04 to $1.4\ \mu\text{m}$, and the mean volume size is $0.47\ \mu\text{m}$. The particles were then rinsed thoroughly with ultrafiltered deionized (DI) water and ethyl alcohol over a 2-week period. After rinsing, the particles were heated at 500°C for 5 h to remove any residual organic compounds.

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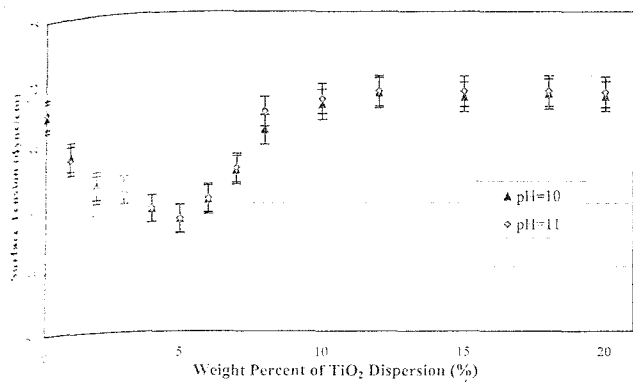


Figure 4. Plot of the surface tension versus weight percent of titania dispersions at pH = 10 and pH = 11. The plot shows that the surface tension of the dispersion decreases significantly from approximately 0% to 5% and then increases above the surface tension of pure water at 10% and higher weight percents.

A charged-stabilized dispersion was created by adding the treated particles to the DI water and adjusting the pH to 10 or 11 with sodium hydroxide (NaOH, Fischer Scientific). The dispersion was stirred for at least 2 h, and the pH was again measured. As the particles adsorbed the charged ions, the pH value would decrease and additional NaOH was added to bring the pH back up to the desired value. The dispersion was again stirred for 2–3 h, and the pH was again measured. This process was repeated several times until a steady pH value was recorded. TiO_2 dispersions with a pH of 10 or 11 were found to be stable for approximately 24 h. Dispersions with a lower pH were typically unstable and, therefore, were not considered in this study.

Surface Tension Measurements. The surface tensions were measured with a Kruss K12 processor tensiometer using a platinum–iridium DeNouy ring. The temperature of the dispersions was kept constant at 30 ± 0.2 °C using a flow-through thermostat unit. The DeNouy ring was thoroughly cleaned before each measurement by first rinsing it with warm tap water, then rinsing it with DI water, and finally cleaning it with concentrated NaOH. Next, the ring was rinsed again with DI water and flamed for several seconds with a Bunsen burner until the ring was red hot, and then it was allowed to cool to room temperature. Before each measurement, the tensiometer was tared and calibrated.

Results and Discussion

The surface tensions versus weight percent of the titania dispersions at pH = 10 and pH = 11 are given in Figure 4. The plot shows that starting from very low weight percents, the surface tension quickly decreases and reaches a minimum around 5 wt %. The surface tension then increases as the weight percent is increased further. In fact, for higher weight percents, the surface tension actually increases to values slightly larger than the surface tension of pure water. The data for pH = 10 and pH = 11 show that the surface tension is relatively insensitive to changes in the pH for high pH values.

Figure 5 is the surface tension of the supernatants of the titania dispersions at pH = 10 for particle weight concentrations from 0 to 6%. The plot shows that the surface tension of the supernatants remains unchanged at different particle concentrations. This result shows that the change of the surface tension of the TiO_2 dispersion is caused solely by the particles and not by contaminants.

As mentioned in the Introduction, we know that the adsorption of the particles to the interface is an energetically favorable process; therefore, spontaneous adsorption of the particles will decrease the energy of the system. Moreover, the adsorption of the particles also changes the entropy of the dispersions. Imagine a colloidal system that is initially void of particles at the interface (Figure 6). The

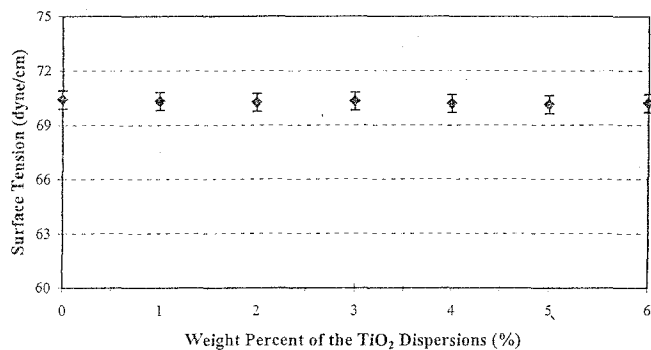


Figure 5. Plot of the surface tension of the supernatants of titania dispersions at pH = 10 and 30 °C. The plot shows that the surface tension of the supernatants is not a function of the particle concentrations.

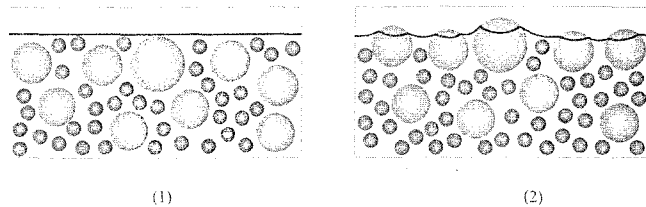


Figure 6. Schematic representation of colloidal particles at the interface (1) before adsorption and (2) after adsorption. After adsorption of the particles to the interface, the internal energy decreases, $U_1 > U_2$, and the entropy increases, $S_1 < S_2$. Therefore, the total free energy decreases, $F_1 > F_2$, which decreases the interfacial tension.

solvent molecules are quite small compared to the colloidal particles and therefore have a greater amount of entropy (i.e., Brownian motion). As colloidal particles begin to insert themselves into the interface and displace the solvent molecules, the average entropy of the interface will decrease. However, as the colloidal particles move from the bulk fluid to the interface, this will create more free volume for the solvent molecules and therefore the entropy of the whole system should increase.

The combined decrease of the total internal energy, U , and the increase in the total entropy, S , cause the total free energy of the system, $F = U - TS$, to decrease. Using the thermodynamic definition of the interfacial energy (eq 4),¹⁵ we see that these two effects cause the surface tension to decrease.

$$\gamma \equiv \frac{\partial F}{\partial A} \quad (4)$$

As the particle concentration at the interface increases, the particles become highly packed and colloidal crystals can form at the interface if the particle size distribution is relatively monodisperse. In our experiments, the particles are not very monodisperse, and well-ordered colloidal crystals are not expected. Nonetheless, we believe that at higher particle concentrations, the particles adjacent to the particles at the interface will push these particles further into the interface. This creates a situation similar to the immersion of particles (Figure 2b) where the attractive capillary force is significant even for very small particles. Furthermore, at high concentrations, the multipole interaction between particles will also be appreciable. As the particles become closer, the capillary forces between the particles will increase dramatically and become quite high and somewhat uniform across the

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interface. The capillary forces between the particles will resist deformations of the interface (i.e., the stretching of the interface during the tensiometric measurements) and therefore increase the effective surface tension. However, when the adsorption of the particles at the interface reaches a saturated state, the capillary force will no longer increase. Therefore, at higher concentrations, the surface tension of the colloidal dispersion will not change with an increase in the concentration as our experimental data show.

To further explain the increase in the surface tension for high particle concentrations, we can look at the Helmholtz free energy of the interface. By definition, the Helmholtz free energy, F , is given as

$$F = U - TS \quad (5)$$

We define F^s as the Helmholtz free energy of the interface and F^b as the free energy of the bulk. The change in F^s is therefore

$$dF^s = dU^s - T dS^s - S^s dT = dQ^s + dW^s - T dS^s - S^s dT \quad (6)$$

where dQ^s is the reversible change of thermal energy with the bulk phases. From the second law of thermodynamics, we can write

$$T dS^s = dQ^s + dQ_{\text{irr}}^s \quad (7)$$

where dQ_{irr}^s/T is the irreversible increase in entropy of the interface. Combining and simplifying the above equations gives us

$$dF^s = -S^s dT - dQ_{\text{irr}}^s + dW^s \quad (8)$$

If we assume the area of the interface changes isothermally and reversibly and use the definition of the surface tension, we arrive at the following relation.

$$\gamma \equiv \left(\frac{\partial F}{\partial A} \right)_{T, \text{irr}} = \left(\frac{\partial F^b}{\partial A} \right)_{T, \text{irr}} + \left(\frac{\partial F^s}{\partial A} \right)_{T, \text{irr}} = \left(\frac{\partial F^b}{\partial A} \right)_{T, \text{irr}} + \left(\frac{\partial W^s}{\partial A} \right)_{T, \text{irr}} \quad (9)$$

Because F^b is not a function of the surface area, A , we get

$$\gamma = \left(\frac{\partial W^s}{\partial A} \right)_{T, \text{irr}} \quad (10)$$

We can now see that as the particle concentration at the interface increases, the interparticle forces per unit area will also increase. The increase in the force per unit area leads to an increase in the amount of work, W^s , it will take to change the surface area. This leads finally to an increase in the surface tension, as seen for higher dispersion concentrations in Figure 4.

Figure 7 is the surface tension of the TiO_2 dispersion versus time at $\text{pH} = 10$. The plot shows that, similar to surfactant solutions, the equilibrium surface tension of the colloidal dispersion is not achieved instantaneously. When a fresh interface is formed, it takes time for the particles to diffuse to the interface and then adsorb onto the interface. Our data show that it takes at least 20 min for the surface tension to reach equilibrium. Even after 1400 s, the surface tension of the dispersions keeps decreasing slowly with time. Actually, we have measured

the dynamic surface tension of the dispersions for surface weight percents as long as 2000 s. The surface tension at 2000 s is a bit smaller than the surface tension at 1400 s, but the difference is very small and within measurement error. When pure water is exposed to air, its surface tension will keep decreasing slightly because of continual contamination. For example, the plot of the surface tension of the supernatant versus time (Figure 7f) shows that the surface tension continues to decrease after 700 s and does not appear to reach a steady state. We would expect the same behavior in the dispersions. Therefore, it is difficult to get an absolute "equilibrium" surface tension of dispersions. In our experiments, we took the average value of five points about 1400 s as the equilibrium value of each measurement.

There may be two mechanisms of particle adsorption at the surface: the diffusion-controlled mechanism and the mixed kinetic-diffusion model.¹⁶ The diffusion-controlled mechanism assumes the particles diffuse from the bulk into the subsurface, and once in the subsurface the particles directly adsorb into the interface. In the mixed kinetic-diffusion model, the diffusion process from the bulk to the subsurface is the rate-controlling step. The mixed kinetic-diffusion model assumes that the particles diffuse from the bulk to the subsurface, but the rate-controlling process is the transfer of these particles to the interface. Once the particles have diffused to the subsurface, there may be an adsorption barrier that prevents the particles from adsorbing. This barrier may be due to increased surface pressure, fewer available adsorption sites, or steric restraints. The existence of the adsorption barrier will cause the particles to diffuse back into the bulk rather than adsorbing, thereby increasing the time scale to reach equilibrium.

If the adsorption of TiO_2 particles is diffusion-controlled, the rate at which the particle equilibrium is gained is controlled by the particle diffusivity, given for dilute solutions by¹⁷

$$D = \frac{k_B T}{6\pi\eta_s a} \quad (11)$$

where η_s is the viscosity of the solvent, k_B is Boltzmann's constant, and a is the radius of the particles. The time for a particle to move a distance d is therefore

$$t_D \approx \frac{d^2}{D} = \frac{6\pi\eta_s d^2 a}{k_B T} \quad (12)$$

If the radius of the particles is $0.5 \mu\text{m}$, the viscosity of the water is 1.1 cP, and the temperature is 300 K, the time t for a particle to move 0.025 mm (the average distance between the particles when the particle weight percent is 10) is about 80 s, which is much less than the time scale that it takes for the surface tension to reach equilibrium. Therefore, it is reasonable to assume that the mechanism of the dynamic surface tension is mixed kinetic-diffusion controlled.

Conclusions

The results presented in this paper show that the surface tension of a colloidal dispersion can be a strong function of the particle concentration. At lower concentrations, the spontaneous adsorption of particles to the surface will

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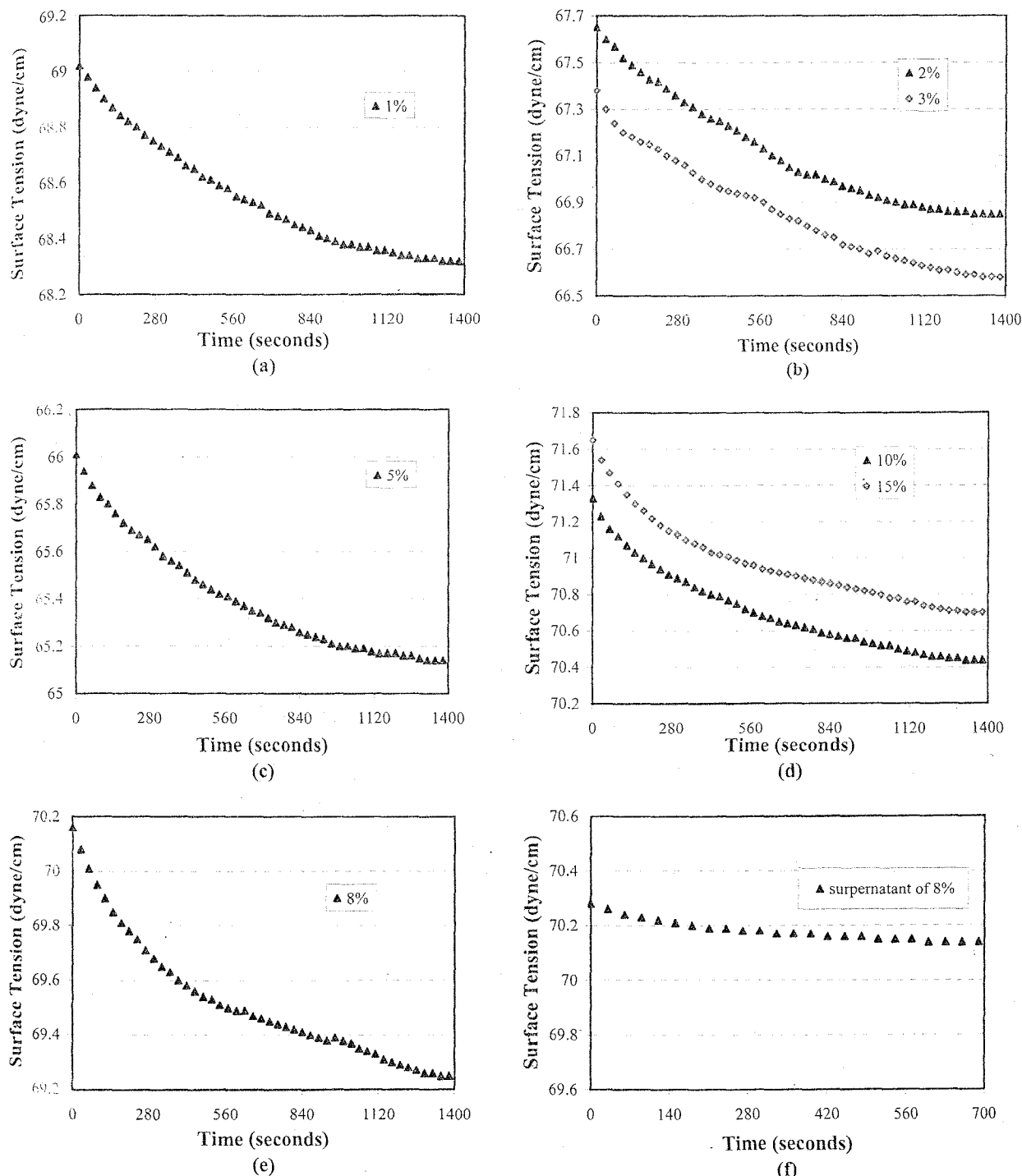


Figure 7. Plot of the surface tension of TiO_2 dispersions versus time at $\text{pH} = 10$ and $30\text{ }^\circ\text{C}$: (a) for 1%, (b) for 2% and 3%, (c) for 5%, (d) for 10% and 15%, (e) for 8%, and (f) for the supernatant of 8%. The plot shows that the particle adsorption at the interface is a dynamic process.

decrease the internal energy and increase the entropy of the system, which lowers the surface tension of the colloidal dispersion. However, due to the existence of the attractive capillary force between the particles, the surface tension will increase with a further increase in the particle concentration. At higher weight percents, the surface tension increases to values close to that of pure water and is no longer a function of particle concentration. This phenomenon is important in explaining the results of Casson and Johnson,⁵ where a dilute suspension of neutrally buoyant particles was seen to cause significant capillary flow.

Our experimental results also showed that the surface tension of the colloidal dispersions is a dynamic process. The calculation of the diffusivity shows that it is very reasonable to regard the dynamic surface tension of the dispersion as a mixed kinetic-diffusion controlled process.

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