

Surface Tension **Studies**



in Colloidal Unimolecular Polymers

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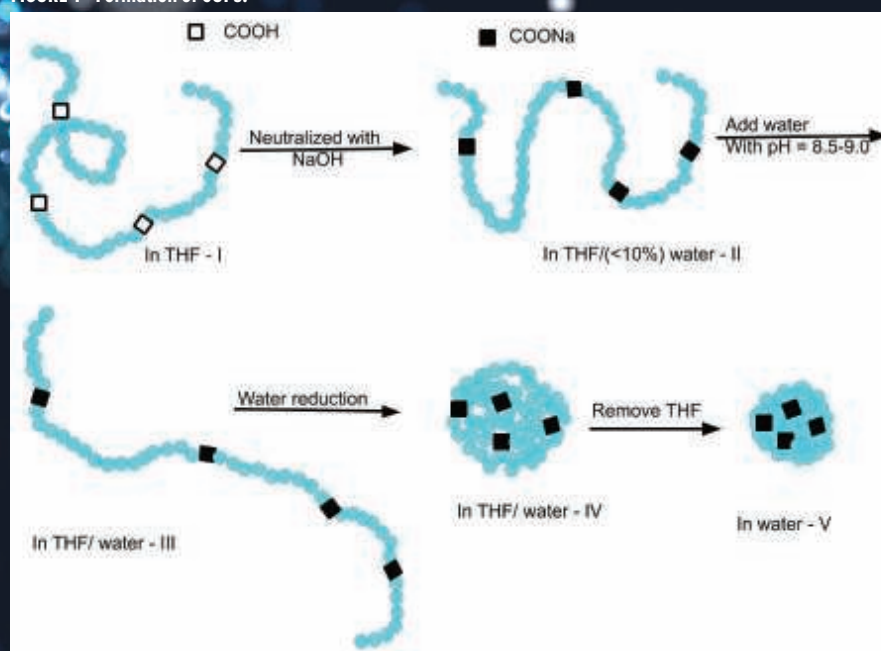
Colloidal unimolecular polymer particles, or CUPs, are true nanoscale charged particles of size less than 10 nm that are made by a simple and easy method, which allows for preparation of additive-free, zero-volatile organic content (VOC) and stable dispersions.¹ These CUP particles are made from a single polymer chain containing a well-balanced number of hydrophobic and hydrophilic units (Figure 1). The polymer chain is transformed into a CUP particle because the polymer-polymer interaction exceeds polymer-solvent interaction during the addition of water to the polymer in dilute solution in a low-boiling, water-loving solvent, resulting in collapse of the chain to form a particle.

This process is similar to formation of micelles, or the water reduction process in water-reducible coatings.¹ The charged groups on the surface of the particles provide stability and prevent aggregation due

to ionic repulsion. The CUP suspension is free of any additives or surfactants as it contains only charged particles, water, and counterions. Due to the process simplicity, it is easy to control the particle size, charge density on the surface, and composition of these particles.² CUP particles can also be a good model material for study of protein due to similarities in their size. They can also have potential applications in the field of coatings, drug delivery, catalyst matrix, etc.

CUPs have a great potential in the field of coatings as demonstrated in several publications by Van De Mark et.al. They can be used as coating resin in conjunction with latex and polyurethane dispersions (PUDs) and can be cured with an aziridine³ or a melamine crosslinker⁴. CUPs with sulfonic acids as the charged stabilizing group can be used as a catalyst for waterborne curing such as acrylic-melamine systems.⁵

FIGURE 1—Formation of CUPs.



CUPs with amine functional groups have been synthesized and used as a crosslinker for waterborne epoxy coatings.⁶ The CUP particles are hydrated with a layer of water around them, often referred to as surface or bound water, which is non-freezable.

Due to the presence of non-freezable water, CUP particles can now be used as additives for freeze-thaw stability and wet edge retention.⁶ Surface tension is very important in paints, and surfactants have long been used to reduce the surface tension of liquid/solvents to improve wetting of pigments and substrate. Like surfactants, CUP particles also have an ability to alter interfacial tension, and it is important to study their interfacial behavior and compare its influence to that of other resin systems that have an excellent history in coatings, such as latex or PUDs.

The surface behavior of small-charge, stabilized particles like silica⁷, polystyrene⁷, and titanium dioxide⁸ have been widely studied. Paunov⁹ has developed a thermodynamic model and relationship for adsorption of charged colloidal particles at the air-water interface. These studies describe the adsorption behavior of the charged particles at the air-water interface, but the particle size of these suspensions are more than 30 nm in diameter. Surface tension studies of truly nanoscale (particle size less than 10 nm) charge-stabilized particles have been rarely reported. This is due to difficulties in making stable suspensions containing only nanoparticles without any other ingredients. Some nanoscale dispersions that have been successfully studied include inorganic particles like silica^{7,10}, bismuth telluride¹¹, and fullerene¹², dispersed in toluene.

In this present work, the surface tension behavior of CUP particles of different sizes, charge densities and different charge stabilizing groups will be studied. The paper will look at the equilibrium as well as the dynamic surface tension behavior of the CUP suspension using a maximum bubble pressure tensiometer. The interfacial behavior of the CUPs will be compared with latex and PUDs, which are the common resins used in the waterborne coatings. In equilibrium surface tension, there is enough time for surfactant to reach equilibrium at the air-water

interface during the measurement. This is achieved by using very slow bubble rate. In dynamic measurement, the bubble rate is varied from slow to fast, and surface tension is measured for each bubble rate. This gives a surface tension vs surface age (related to bubble rate) profile with information about the migration and diffusion behavior of the surfactant, or in this case, CUP particles. The surface tension was measured using the maximum bubble pressure method, which allows both dynamic and equilibrium surface tensions to be measured without the effects of humidity, air turbulence, and contamination of carbon dioxide. Other common methods are the Du Noüy ring method, oscillating jet method and drop methods.

EXPERIMENTAL

Synthesis of Polymer and Water Reduction

The carboxylate (anionic) functional polymers (Polymer 1 and 2) were synthesized and reduced using procedure mentioned in reference (1). The monomer ratio of methyl methacrylate (MMA) to methacrylic acid (MAA) was 9:1 for both the polymers. The amounts of 1-dodecanethiol used was 0.82 g and 0.33 g for 28K and 60K polymer, respectively. The sulfonate (anionic) functional polymer (Polymer 3) was synthesized and reduced using procedure mentioned in reference (5). The monomer ratio of MMA to AMPS (2-acrylamido-2-methylpropane sulfonic acid) was 9:1. The molecular weights of the polymers were controlled by using chain transfer agent n-butanethiol (0.14 g). The QUAT (cationic) functional polymer (Polymer 4) was synthesized and reduced using the procedure mentioned in reference (13). The monomer ratio of MMA to QUAT ([2-(methacryloyloxy) ethyl] trimethylammonium chloride) was 9:1. The latex and PUDs used in this study were obtained from commercial sources. The latex was diluted to 24% solids using water before making measurements. Two PUDs were used for this study: PUD1 has no solvents or surfactant, while PUD2 contains coalescing aid (N-methylpyrrolidone, or NMP). Both the PUDs were diluted to 24% using water. The PUD2 has 12.9% NMP at resin concentration of 24% solids.

Characterization

The absolute molecular weights and distribution of the copolymers were measured by gel permeation chromatography (GPC) using a Viscotek model 305 from Malvern Corp. The GPC instrument was equipped with a triple detector array (refractive index detector, low- and right-angle light scattering detector, and intrinsic viscosity detector), thus yielding absolute molecular weight. The flow rate of tetrahydrofuran was 0.5 ml/min, and the injection volume 100 μ l. The acid numbers of copolymers were measured by the titration method found in ASTM D 974 that was modified by using potassium hydrogen phthalate (KHP) instead of hydrochloric acid, and phenolphthalein instead of methyl orange. The titration was performed in tetrahydrofuran as the solvent for carboxylate copolymer and in methanol for sulfonate copolymer.

The CUP suspensions were dried at 50° C under vacuum in presence of solid sodium hydroxide to absorb carbon dioxide. The clear crystal-like material was then heated at 110° C until constant weight was obtained. The density of the CUP was measured by a gas displacement pycnometer, Micrometrics AccuPycII 1340. Equilibrium flow rate of Helium gas is 0.005 psig/min, and temperature was controlled at 25.89 \pm 0.04° C. Twenty-five readings were made for each sample, and the results were reported by its average and standard deviation. The particle size of the CUPs was measured by dynamic light-scattering (DLS) technique using the Microtrac Nanotrak 250. The viscosity of the suspension was used instead of water viscosity in order to compensate for the change in diffusion coefficient due to viscosity increase caused by the charged groups on the surface of CUP particles.¹ The particle size of latex and PUDs was measured using the regular procedure (i.e., using the viscosity of water).

Sensadyne PC-500 LV was used to measure the surface tension of CUP suspensions. Suspensions were equilibrated in a constant temperature water bath at 25 \pm 0.1° C. The tensiometer was calibrated with analytical reagent 100% absolute ethanol and Milli-Q ultrapure water. Flow rate of nitrogen gas was 40 ml/min and flow pressure was maintained at 25 psi. An average of three readings with less than 0.1 dyn/cm difference was reported. The surface age used for measuring the

equilibrium surface tension was 3 sec. For dynamic surface tension, the maximum and minimum bubble rate were determined as the rate beyond which the surface tension did not change.

RESULTS AND DISCUSSION

Characterization of Polymers

Table 1 shows the acid number, density, and molecular weight of the copolymers. There is an increase in the density of the dry CUPs as the molecular weight increases due to decrease in the weight fraction of the end groups with increasing molecular weight.¹⁴ The density observation was consistent with the molecular dynamic simulation result of a Leonard-Jones model with fixed bond length reported by Leporini et al.¹⁵ The molecular weights of Polymer 1 and Polymer 2 were measured using gel permeation chromatography (GPC) technique. The molecular weights of Polymer 3 and Polymer 4 were calculated from the particle size of the CUPs using the equation relating molecular weight and particle size of globular proteins, assuming a perfect sphere shape for the CUP particles. The equation was expressed as:

$$MW = \frac{\pi d^3 \rho_p N_A}{6} \quad (1)$$

where N_A = Avogadro's number and ρ_p is the CUP density.

Particle Size Analysis

The CUP suspensions were filtered through a 0.45- μ m Millipore membrane filter before performing particle size measurement. Table 2 shows the measured particle size for the copolymers, calculated particle size from molecular weight for Polymers 1 and 2 and calculated molecular weight from particle size for Polymers 3 and 4. The diameter of the CUP particles was calculated from its molecular weight using Eq. (1). These results are consistent with size dependence of globular proteins on their molecular weight [16] and our previous work [2]. The distribution of molecular weight of the polymer gives the same distribution to the particle size of the CUPs.

Equilibrium Surface Tension Behavior

Latex and PUDs often contain additives, surfactants, coalescing aid, or cosolvents, which makes it difficult to study the

properties of the nanoparticle by itself. In order to purify them, complicated and lengthy procedures like dialysis need to be done. These additives can also

show interfacial behavior along with the nanoparticle. Figure 2 shows the surface tension behavior of pure PUD resin (PUD1) containing no solvents or

TABLE 1—Acid number, densities, and molecular weights of the copolymers

SAMPLE ID	MONOMER RATIO	MEASURED ACID VALUE ^a	ρ_p ^b	Mn ^c	Mw/Mn
Polymer 1 (Carboxylate functional)	MMA:MAA = 9:1	56.8	1.2250 ± 0.0018	28,900	1.83
Polymer 2 (Carboxylate functional)	MMA:MAA = 9:1	57.0	1.2310 ± 0.0014	59,800	1.73
Polymer 3 (Sulphonate functional)	MMA:AMPS = 9:1	46.9	1.2016 ± 0.0020	56,000	
Polymer 4 (QUAT functional)	MMA:QUAT = 9:1	N.A.	1.1751 ± 0.0012	55,000	

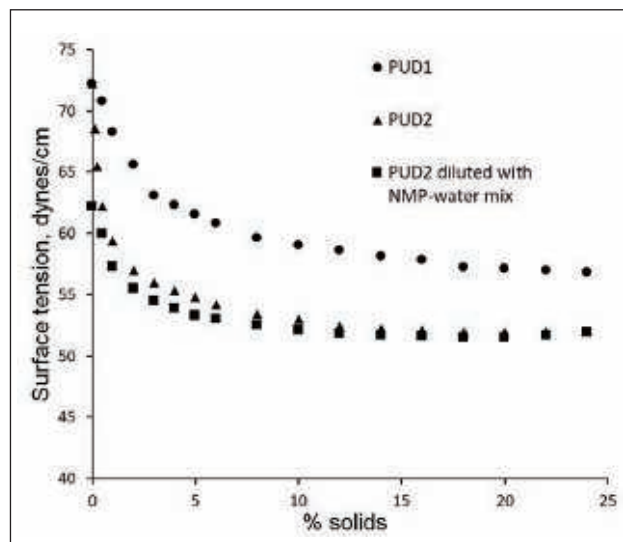
- a) Acid number from ASTM D 974, mg KOH/g ; Calculated acid number for Polymers 1 and 2 is 56.9 mg KOH/g; calculated acid number for Polymer 3 is 46.8 mg KOH/g
 b) Density of dry CUPs (g/cc) at 25.89 ± 0.04° C except Polymer 1 at 24.38 ± 0.03° C.
 c) Molecular weights of Polymers 1 and 2 were measured using GPC. Molecular weights of Polymer 3 and 4 were calculated from particle size measurements (d = diameter) using Eq. (1)

TABLE 2—Molecular weights and particle size of the CUPs

SAMPLE ID	Mn ^a	Mw/Mn	d(DLS) ^b (nm)	d(GPC) ^c (nm)
Polymer 1	28,900	1.83	3.4	3.5
Polymer 2	59,800	1.73	4.2	4.2
Polymer 3	56,000		5.3	
Polymer 4	55,000		5.6	
Latex			140.0	
PUD1			30.0	
PUD2			24.6	

- a) Molecular weights of Polymers 1 and 2 were measured using GPC. Molecular weights of Polymers 3 and 4 were calculated from particle size measurements [d(DLS) = diameter] using Eq. (1).
 b) Diameters measured by dynamic light scattering (DLS) instrument.
 c) Diameters calculated from average molecular weight measured using gel permeation chromatography (GPC)

FIGURE 2—Surface tension vs concentration behavior for PUD1 (solid circles ●), PUD2 (solid triangles ▲) and PUD2 (solid squares ■) diluted to different concentration using 12.9% NMP-water mixture instead of water.



surfactants (solid circles ●) as well as PUD resin (PUD2) containing a coalescing aid NMP (N-methyl pyrrolidone) (solid triangles ▲) at different concentration prepared by diluting with DI water. Comparing the two plots, one can see the difference in the slopes of the curves, especially at lower percent solids. This is because small amount of NMP can cause large reduction in surface tension of water. The surface tension behavior of water-NMP mixture is not linear and is more pronounced at lower weight fractions. The pure PUD resin at highest dilution of 0.5% solids has surface tension of 71 dyn/cm, which is close to that of water, 72.2 dyn/cm, and with any further dilution the surface tension will approach that of water. However, the PUD resin with NMP at 0.5% solids shows much lower surface tension (i.e., 62.2, which is far from that of water). Even at much lower concentration of 0.125% solids, the surface tension (68.5 dyn/cm) does not approach that of water. This behavior is due to the presence of NMP, which has significant effect on surface tension of water even at low concentrations. Another approach to study the behavior of a PUD resin having NMP or other cosolvents is to dilute the resin such that the concentration of NMP is the same at different concentration of PUD. This is shown in the *Figure 2* (solid squares ■), where the different percent solids of PUD resin (PUD2) was prepared by diluting with 12.9% of NMP-water mixture instead of regular DI water. The PUD resin (PUD2) at 24% resin solids had 12.9% NMP in it, which was kept constant by diluting it with NMP-water mixture of same concentration. The curve (solid squares ■), therefore, shows the behavior of PUD2 at different concentrations by eliminating the effect of NMP. The surface tension values at low percent solids seems to approach that of 12.9% NMP-water mixture (62.1 dyn/cm) as expected. However, this method is not ideal because the concentration of free NMP present in the water is dependent on the percent solids of PUD present. NMP is a coalescing aid and should therefore partition inside the PUD particles. This will reduce the amount of free NMP present in water that can influence the surface tension. One needs to know the partitioning behavior at all concentration to be able to eliminate the effect of NMP.

Figure 3 shows the surface tension behavior of latex, pure PUD, and CUPs.

The latex used has not been purified to remove the impurities, which could have influenced the surface tension behavior of the system. The latex and PUD show lower surface tension values than CUPs at all concentration, whereas PUD has higher values from 4% solids onwards and similar values at lower concentrations. In general, these differences can be related to the particle size of the three systems.

The higher the particle size, greater is the reduction in surface tension. The similar values between latex and PUDs can be explained by the presence of impurities in the latex, which include residual surfactant and additives. Without the knowledge of the type of impurities and their amounts, it is difficult to explain the behavior of latex. CUPs, on the other hand, are free of additives, and their behavior, shown in *Figure 3*,

FIGURE 3—Surface tension vs concentration behavior for Polymer 2 (CUPs) (solid circles ●), PUD1 (solid triangles ▲) and latex (solid squares ■).

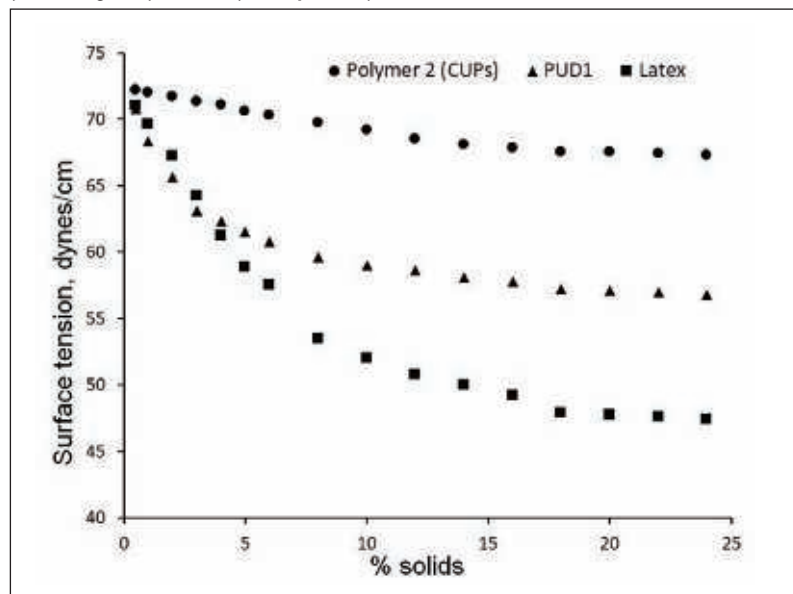
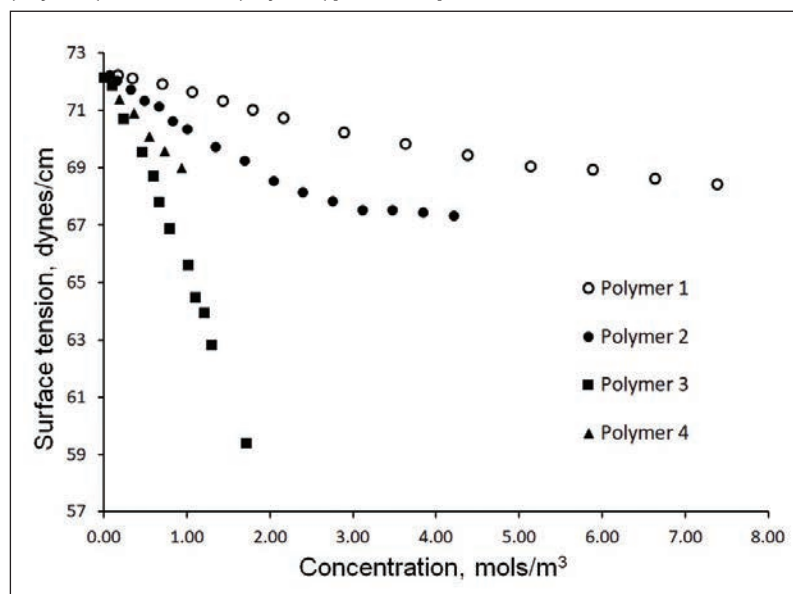


FIGURE 4—Equilibrium surface tension of the carboxylate CUPs (Polymers 1 and 2), sulfonate CUPs (Polymer 3), and QUAT-CUPs (Polymer 4) [reference 13].



is entirely due to the effect of particles present at air-water interface.

The equilibrium surface tension of the carboxylate CUPs, sulfonate CUPs and QUAT-CUPs decreases at low concentrations linearly with increasing concentration as seen from *Figure 4*. This behavior of reduction in surface tension with increasing concentration is also observed for typical surfactants. Increasing the CUP concentration increases the concentration of counterions and leads to Manning condensation (i.e., condensation of counterions on the CUP surface). The phenomenon of counterion condensation causes the reduction of effective surface charge making it lower than the bare surface charge. The reduced surface charge allows a greater number of CUP particles with a better packing at the air-water interface thereby increasing the total number of charged groups at the air-water interface since only a small fraction of the charged group undergo Manning condensation. This leads to increased electrostatic repulsion at the interface, which reduces surface energy of the system.

The equilibrium surface tension of the carboxylate CUPs decreases with increasing the molecular weight (size) from 28K (Polymer 1 – 4.2 nm) to 60K (Polymer 2 – 5.4 nm). Similar behavior has been observed by Okubo⁷, where the surface activity of methyl polyethylenimine increased with increasing molecular

weight. Okubo attributed this behavior to the increase in hydrophobicity of the backbone with increasing molecular weight. In the case of CUPs, reduction of surface tension with increasing molecular weight could be due to an increase in the number of charged groups on the surface of the CUP particles with increasing molecular weight. The individual polymer chain is composed of 9:1 ratio of MMA ($M_w = 100$): MAA ($M_w = 86.06$) for the carboxylate Polymers 1 and 2. There is one carboxylate group every 986 Da of polymer. Therefore, the number of charged groups present per particle for Polymer 1 is 28 and Polymer 2 is 61. The charge density can be calculated for CUP particles made from Polymer 1 and 2 using equation (2). The charge density (in ions/nm²) for CUP particles made from Polymer 1 and 2 is 0.52 and 0.66, respectively. The change in the surface energy caused by particles at the interface can be due to attractive (van der Waals) or repulsive (electrostatic) forces between them. When the van der Waals force increases, there is an increase in the surface energy and consequently an increase in surface tension since more work is required to distort the surface. CUP particles have charged groups, either anionic (carboxylates and sulfonates) or cationic (QUAT), that repel each other when adsorbed at the air-water interface and can possibly reduce the surface energy of the system, therefore lowering

the surface tension. CUP particles with higher molecular weight have lower surface tension because of higher electro-repulsion due to the presence of more charged groups per unit area on the surface.

$$\sigma = \frac{M_{CUP}}{4\pi r^2 (n \times M_{MMA} + M_{MAA})} \quad (2)$$

σ is the charge density in ions/nm², r is the radius of the CUP, n is the monomer ratio ($n:1$ of MMA:MAA), M_{CUP} is the molecular weight of the CUP, M_{MMA} is the molecular weight of MMA, M_{MAA} is the molecular weight of MAA.

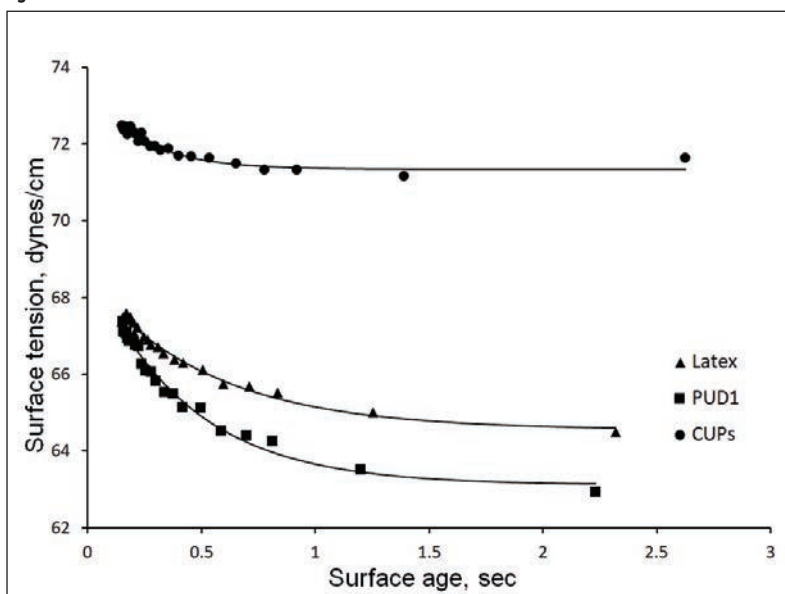
The effect of size on surface tension is also observed in latex and PUDs, as discussed earlier. But it is difficult to relate the behavior to charge density because, in the case of latex and PUDs, it is not possible to determine the number of charges present on each particle. The CUP particle was designed such that when the polymer collapses, it forms a particle from a single chain and the hydrophobic groups to fold in and form the interior of the particle, leaving the hydrophilic groups on the surface. It is therefore possible to calculate the number of charges present on the surface of the particle. The PUDs are large in size and are formed by collapse of multiple polymer chains to a particle. Many of the hydrophilic groups on the polymer chain get buried inside the particle, and the number of groups present on the surface is unknown. This makes it harder to calculate the charge density of the particle.

The sulfonate CUPs show greater reduction in surface tension as compared to carboxylate CUPs and QUAT-CUPs. This can be explained by contact angle reduction due to particles at the interface. As the surface tension is reduced, the contact angle of the adsorbed particles at the interface also decreases.^{17,18} The work of Okkema and Cooper¹⁹ have shown that the sulfonate group, being more polar and hydrophilic than the carboxylate, gave lower contact angle at the air-water interface. The QUAT CUPs show similar reduction in surface tension as the carboxylate CUPs, which is due to similar polarities of the hydrophilic quaternary ammonium group and carboxylate group.

Dynamic Surface Tension Behavior

Figure 5 shows the dynamic surface tension behavior of the latex, PUD1, and

FIGURE 5—Dynamic surface tension behavior of the latex, PUD1, and CUPs at different surface ages at 3% solids.



CUPs by plotting the surface tension against the surface age at concentration of 3% solids. Surface age is defined as the time interval between the onset of bubble growth and the moment of maximum pressure. When there is an increase in surface age, the bubble rate is slow, which gives the CUP particles more time to reach the air (bubble)-water interface. The time to reach equilibrium is the longest for latex, which is then followed by PUDs and then by CUPs. The kinetically limited adsorption (KLA) model reported by Diamant and Andelman²⁰ explains such exponential relaxation of surface tension. According to Andelman et al., the kinetic relaxation time τ_k was indicative of electrostatic potential at the surface, which gave rise to electrostatic repulsion. As seen from the values in Table 3, the τ_k increases with increasing molecular weight which indicates a barrier to surface adsorption via electrostatic repulsion, thus slowing the adsorption of CUP particles to the interface.

The data has an exponential fit represented by equation (3). The fitting parameters are shown in Table 3.

$$\gamma - \gamma_e = A \times \exp\left(\frac{-t}{\tau_k}\right) \quad (3)$$

Where γ_e is the equilibrium surface tension and A and τ_k are fitting parameters.

Accurate particle size of the CUP particles can be measured using DLS method while replacing the solvent viscosity with the solution viscosity to compensate for increased viscosity due to electroviscous effect. For latex and PUD, viscosity of water is used and not viscosity of solution. The collective diffusion coefficient can be calculated from the generalized Stokes-Einstein model for the diffusion of spherical particles expressed as equation (4), which relates the collective diffusion coefficient to the radius of the particle (r) measured using DLS and the viscosity of the solution (η) at 25° C.

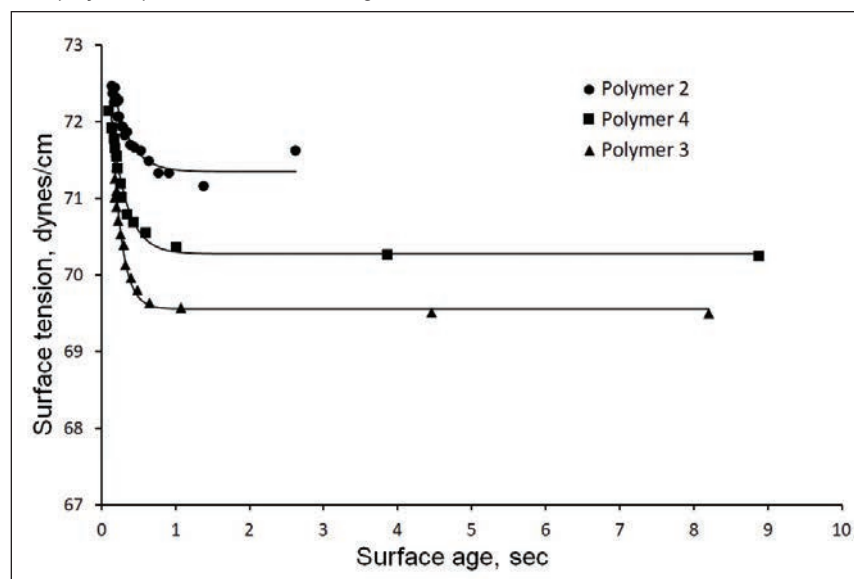
$$D_c = \frac{k_b \times T}{6 \times \pi \times \eta \times r} \quad (4)$$

where k_b is the Boltzmann constant, and T is the absolute temperature of the solution. The diffusion coefficients at 25° C calculated (each at a volume fraction of 0.05) for the CUP polymers, latex, and PUD1 are mentioned in Table 3. The values of diffusion are very low for latex and PUDs due to

TABLE 3—Fitting parameters for dynamic surface tension vs surface age at 0.5 mol/m³ and diffusion coefficient (D_c) at 25° C

SAMPLE ID	γ_e	A	τ_k	ADJ. R ²	D_c (10 ⁻⁶ cm ² /s)
Latex	64.55	3.93	0.53	0.984	0.03
PUD1	63.11	5.88	0.42	0.927	0.12
Polymer 2	71.34	2.22	0.23	0.984	0.51
Polymer 3	69.56	7.52	0.13	0.985	0.66
Polymer 4	70.27	3.32	0.21	0.95	0.45

FIGURE 6—Dynamic surface tension behavior of the carboxylate (Polymer 2), sulfonate (Polymer 3), and QUAT (Polymer 4) CUPs at different surface ages.



their large size. This explains the longer time taken by them to reach equilibrium surface tension since they diffuse slowly to the air-water interface.

Figure 6 shows the dynamic surface tension behavior of carboxylate, sulfonate, and QUAT CUPs by plotting the surface tension against the surface age at concentration of 0.5 mol/m³. Both QUATs and carboxylates require a similar amount of time to reach equilibrium surface tension. They both reach equilibrium surface tension at surface age of 1.5 sec. This could be because they have similar diffusion coefficients and similar polarities of their hydrophilic groups. Sulfonates show much faster relaxation time, which could be due to higher polarity of its hydrophilic group.

CONCLUSION

Colloidal unimolecular polymers with anionic (carboxylates and sulphonates)

and cationic group on surface were successfully made and studied to understand their equilibrium and dynamic behavior. These CUP suspensions had a true nanoscale size (3-9 nm) and zero-VOC due to complete removal of solvent. The CUP particles have surface water associated with it as do the latex and PUDs. However, the CUPs have a higher volume fraction of surface water associated with it than PUDs and latex. In the case of CUPs, the thickness of the water layer is comparable to the radius of the CUP particles, whereas for latex and PUDs, the thickness is much smaller compared to the radius. Due to the presence of this thick bound water layer, the CUP particles behave as a larger particle than their actual size. The equilibrium surface tensions of latex, PUDs and CUPs show that the surface tensions decrease as the size increases at a fixed concentration. The presence of impurities and cosolvents can affect

the surface tension behavior as shown in the case of PUD resin containing NMP (PUD2). The sulfonate CUPs show lower surface tension than QUATs and carboxylates due to differences in the polarities of the hydrophilic groups. CUPs show an increase in surface tension with increase in size, which could be attributed to the increase in surface charge density. The dynamic surface tension reveals the effect of size on the time required to equilibrium surface tension. As the size increases, the diffusion becomes slower, and more time is required to reach the equilibrium surface tension. Further study of CUPs with different molecular weight but same charge density would elucidate impact of charge density on the surface tension. The effect on surface tension as the charge density increases, and also the effect of concentration where Manning condensation (i.e., counterion condensation) begins needs to be investigated. ❄

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