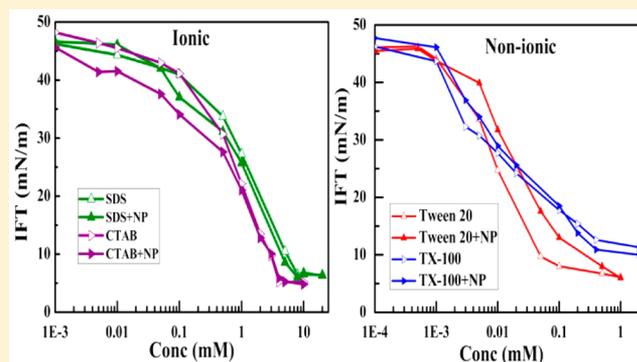


# Effect of Different Surfactants on the Interfacial Behavior of the *n*-Hexane–Water System in the Presence of Silica Nanoparticles

Nihar Ranjan Biswal, Naveen Rangera, and Jayant K. Singh\*

Department of Chemical Engineering, Indian Institute of Technology Kanpur, Kanpur 208016, India

**ABSTRACT:** This paper presents the effect of negatively charged silica nanoparticles (NPs) on the interfacial tension of the *n*-hexane–water system at variable concentrations of four different surfactants, viz., an anionic surfactant, sodium dodecyl sulfate (SDS), a cationic surfactant, cetyltrimethylammonium bromide (CTAB), and two nonionic surfactants, Tween 20 and Triton X-100 (TX-100). The presence of negatively charged silica nanoparticles is found to have a different effect depending on the type of surfactant. In the case of ionic surfactants, SDS and CTAB, silica NPs reduce the interfacial tension of the system. On the contrary, for nonionic surfactants, Tween 20 and TX-100, silica NPs increase the interfacial tension. The increasing/decreasing nature of the interfacial tension in the presence of NPs is well supported by the calculated surface excess concentrations. The diffusion kinetic control (DKC) and statistical rate theory (SRT) models are used to understand the behavior of dynamic interfacial tension of the surfactant–NP–oil–water system. The DKC model is found to describe the studied surfactant–NP–oil–water systems more aptly.



## 1. INTRODUCTION

Reduction in interfacial tension caused by the spontaneous self-assembly of surfactants or colloidal particles at liquid–liquid interfaces plays an important role in numerous areas of science and engineering for many important technological applications like foam and emulsion stability,<sup>1–7</sup> enhanced oil recovery,<sup>8</sup> wettability,<sup>9</sup> application in phase-transfer catalysis,<sup>10,11</sup> etc.

In recent years there has been an increasing interest in nanofluids, i.e., fluid containing stable suspension of nanometer range particles made of metals, oxides, carbides, or carbon nanotubes, as it carries special thermophysical properties and capability to enhance the mass-transfer rate. Various studies have been done to illustrate the effect of nanoparticles (NPs) on reducing the interfacial tension of several oil–water<sup>12–15</sup> systems aiming for important applications like foam and emulsion stability where reduced interfacial tension enhances the stability of emulsion. In addition, some works on the effect of surface inactive nanoparticles, in the presence of different surfactants, on the interfacial behavior of the oil–water system<sup>16–19</sup> have also been reported. For the latter case, interaction between NPs and surfactant molecules can alter the stability of emulsions, adsorption, and consequently interfacial activity.

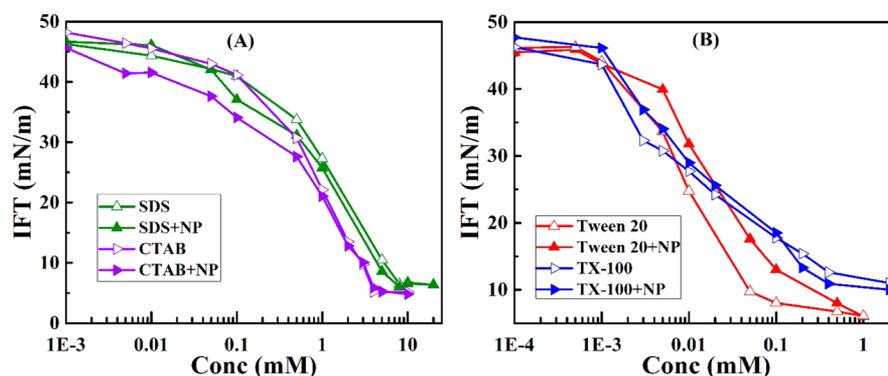
There is still a long ongoing debate on whether NPs adsorbed at an interface can reduce the interfacial tension.<sup>12,14,20–31</sup> Briefly, Okubo<sup>12</sup> investigated the water–air interfacial tension in the presence of polystyrene and silica particles. The interfacial tension was found to reduce significantly in the presence of polystyrene particles. However, in the presence of silica particles at the interface, the interfacial

tension was found to remain practically equal to that of the water–air interface. Dong and Johnson<sup>14</sup> studied the interfacial tension of charge-stabilized TiO<sub>2</sub> dispersion in water at high pH. They observed that as the particle concentration in the system increases, the interfacial tension first decreases. However, a further increase in concentration increases the interfacial tension to values even larger than those observed in the absence of NPs. Vignati and Piazza<sup>21</sup> measured the interfacial tension of an oil droplet in water in the presence of silica NPs treated with hexamethyldisilazane. The interfacial tension was found not to change with the variation of either the NP concentration or the hydrophobicity of their surface. Saleh et al.<sup>22</sup> reported that highly charged poly(styrenesulfonate)-grafted silica particles can significantly reduce water–oil interfacial tension, whereas the bare silica particles do not affect the interfacial tension. Glaser et al.<sup>23</sup> found that Au–Fe<sub>3</sub>O<sub>4</sub> Janus NPs can significantly reduce the interfacial tension compared to the homogeneous ones at similar concentrations. Blute et al.<sup>27</sup> studied the interfacial tensions in the presence of various types of commercial silica NPs, by systematically varying the system pH, hydrophobicity and NP concentration. The authors observed the greatest reduction in interfacial tension for the partially modified particles adsorbed at the interface. Pichot et al.<sup>29</sup> studied the effect of hydrophilic silica particles at the vegetable oil–water interface and found that the presence of the silica particles has no effect on interfacial

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**Figure 1.** Equilibrium interfacial tension of SDS and CTAB (A) and Tween 20 and TX-100 (B) surfactants in the absence and presence of 0.1 wt % silica nanoparticles at the *n*-hexane–water interface. Standard deviations are less than 1%.

tension. Saïen et al.<sup>30</sup> studied the effect of hydrophobic (modified by hexadecanoic acid) and hydrophilic (bare alumina NP) alumina nanoparticles on the toluene–water interface, and they found that the interfacial tension increases in the presence of hydrophilic (bare surface) and decreases in the presence of hydrophobic (modified surface with hexadecanoic acid) nanoparticles.

There are also numerous studies on the effect of NPs on the adsorption of surfactant solutions at air–water and oil–water interfaces.<sup>17–19,29,32–36</sup> Moghadam and Azizian<sup>17</sup> compared the interfacial tension of CTAB in the presence of ZnO nanoparticles at the *n*-decane–water interface to that of pure surfactant. The authors found that interfacial tension further reduces, at a given concentration of surfactant, in the presence of NPs and reaches a value  $\approx 2$  mN/m at critical micelle concentration (CMC) (0.9 mM). The authors observed that the adsorption of surfactants on nanoparticles drives the nanoparticles toward the interface due to the increased hydrophobicity, which is very similar to the kind of result noticed by Ravera et al.<sup>32</sup> Moghadam and Azizian<sup>18</sup> also studied the effect of ZnO nanoparticles on anionic SDS surfactant, at the *n*-decane–water interface and found that the presence of ZnO nanoparticles enhances the efficiency of the SDS molecules to decrease the interfacial tension. Adsorption of both nanoparticles and surfactants at an interface make a synergistic effect for higher reduction of interfacial tension. Moghadam et al.<sup>19</sup> compared the efficiency of two gemini surfactants in reducing the oil–water interfacial tension with and without ZnO nanoparticles. They found that the synergistic interactions between the surfactants and nanoparticles decrease the interfacial tension beyond that observed for each component, alone. The experimental results clearly show that the addition of ZnO nanoparticles increases the efficacy of the surfactants in reducing oil/water interfacial tension. It was found that the 12–3–12 surfactant is more efficient than the 14–3–14 surfactant. Furthermore, the authors have shown that on the basis of the interactions between NPs and surfactants, generally interfacial activity of surfactants increases with NPs.

The above literature survey clearly suggests that nanoparticles sometime alter the liquid–liquid interfacial tension, whereas for other cases nanoparticles solely are found to be surface inactive. Despite many experimental investigations, understanding the effect of different nanoparticles, in the presence/absence of different surfactants and/or other surface-active molecules on interfacial tension of liquid–liquid system is far from complete. A combined comparative study of three types of surfactant, namely, cationic, anionic, and nonionic, in

the presence and absence of charged nanoparticles at the oil–water interface has not been reported earlier. Hence, the aim of the present work is to study the effect of nanoparticles on the interfacial behavior of different surfactants at water–oil (*n*-hexane) interface.

## 2. MATERIAL AND METHOD

**2.1. Materials.** Three different types of surfactants, nonionic [Tween 20 (99% purity) (CMC-0.08 mM), Triton X-100 (TX-100; 99% purity) (CMC-0.15 mM)], cationic [cetyltrimethylammonium bromide (CTAB, 99% purity) (CMC-0.9 mM)], and anionic [sodium dodecyl sulfonate (SDS) (CMC-8 mM)], were used in this work. Tween 20, TX-100, and CTAB were purchased from Loba Chemicals Pvt. Ltd. SDS of technical grade was purchased from Sigma-Aldrich chemicals and used without any further purification. The *n*-hexane (99% purity) used for the oil–water interface was purchased from Rankem. The silica nanoparticles used for this experiments were purchased from Otto chemicals Pvt. Ltd., Mumbai, India. The  $\zeta$  potential of silica nanoparticles was measured by Zetasizer Nano ZS (Malvern, U.K.) and found to be  $-23.63$  mV.

Aqueous solutions of individual surfactants were made by ultrapure water (Millipore India Private Limited) of 18.2 M $\Omega$ -cm resistivity, 71.5 mN/m surface tension, and 6.5–7 pH at 25 °C. For all the experiments a single surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

**2.2. Methods.** **2.2.1. Pendant Drop Tensiometry.** The interfacial tension (IFT) of different surfactants solutions without and with 0.1 weight (wt) % silica nanoparticles in the *n*-hexane–water system were measured at 25 °C by the pendant drop technique<sup>37</sup> using a goniometer (OCA 35, Data physics, Germany). A 30  $\mu$ L volume drop of different concentrations of surfactant solutions without and with nanoparticles was produced at the tip of a stainless steel needle (outer diameter 1.65 mm) immersed in a bulk *n*-hexane phase. A high-speed camera captured the shape of the drop, and the image profile was fitted with the Young–Laplace equation to obtain the interfacial tension ( $\gamma$ ). All the experiments are repeated three times, and average values are given here.

**2.2.2. Nanofluid Preparation.** For the preparation of nanofluid, 0.1 wt % of silica nanoparticles was added to different concentrations of surfactant solution, and the samples were sonicated about 30 min for the proper dispersion. The

same stock was used for the preparation of both surfactant solution and nanofluids.

### 3. RESULTS AND DISCUSSION

**3.1. Effect of Silica Nanoparticles on Interfacial Tension at the *n*-Hexane–Water Interface.** The interfacial tension (IFT) of the *n*-hexane–water system was first measured and found to be 49 mN/m, which is in excellent agreement with the literature.<sup>13,20,31</sup> Subsequently, the interfacial tension of *n*-hexane–water in the presence of silica was measured over a long period of time (850 s). It is observed that with an increase in the weight % of the silica nanoparticle, the IFT remains almost constant for the same period of time. Hence, it is evident that the sole silica nanoparticle has no role in reducing the IFT value of the *n*-hexane–water system, which is similar to the results obtained by many researchers for different hydrophilic as well as hydrophobic nanoparticles.<sup>12,17–19,29,32,33</sup> Now, we turn our attention to the effect of a mixture of silica NPs with different surfactant systems on the interfacial behavior of the *n*-hexane–water system.

**3.2. Effect of Silica Nanoparticles on Equilibrium Interfacial Tension of Different Surfactant Solutions.** Figure 1 presents the equilibrium interfacial tension of the *n*-hexane–water system in the presence of different surfactants, which were measured over a long period of time for two cases, viz., without silica nanoparticle and with 0.1 wt % silica nanoparticle.

It is evident from Figure 1 that with an increase in surfactant concentration, the interfacial tension at the *n*-hexane–water interface decreases for all the surfactants, as expected. However, the effect of nanoparticles on the interfacial tension is distinctly dependent on the type of the surfactant. Adding 0.1 wt % of negatively charged silica nanoparticles in the presence ionic surfactants, SDS and CTAB, further decreases the interfacial tension of the *n*-hexane–water system (Figure 1A). In contrast to the ionic surfactant, nonionic surfactants behave differently where the silica nanoparticle retards the efficiency of surfactant in reducing IFT. In other words, nanoparticles increase the IFT of the *n*-hexane–water system containing nonionic surfactants (Figure 1B). At a very low surfactant concentration, in the absence and presence of silica nanoparticles the change in IFT values is not prominent. However, at a relatively higher surfactant concentration the effect of NP is clearly visible. Furthermore, an increase in the surfactant concentration diminishes the effect of NP, as a sufficient number of surfactant molecules is at the interface to reduce the IFT to a greater extent. In the case of anionic surfactant, SDS, more SDS molecules migrate from the bulk phase to the interface due to the repulsive interaction between negative charged silica NPs and negative charged SDS molecule. As a result, the IFT decreases. On the contrary, in the case of cationic CTAB, due to attraction between oppositely charged silica NPs and CTAB molecules, the CTAB molecules get attached on the surface of the NPs, making the particles hydrophobic. The modified NPs, being hydrophobic, eventually move to the interface, thus effectively reducing the IFT.

To quantify the retarding efficiency of nonionic surfactant, TX-100, in the presence of silica nanoparticles, we have studied the effect of different weight % of nanoparticles on the IFT of 0.02 mM (~10 times lower than CMC) TX-100 surfactant, which is summarized in Table 1.

Table 1 clearly illustrates that with increase in weight % of silica nanoparticle from 0.01 to 1 wt %, the IFT value increases

**Table 1. Variation of IFT with the Change in Weight % of Nanoparticles**

weight % of NPs	minimum IFT (mN/m)
0	23.77
0.01	24.04
0.1	24.60
0.2	25.33
0.5	24.89
1	25.42

from 23.77 mN/m (for pure 0.02 mM TX-100) to 25.33 mN/m (for 0.2 wt %). The subsequent increase in concentration (up to 1 wt %) of nanoparticles has very little effect on the IFT values. This is because the silica nanoparticles block the transportation of TX-100 surfactant molecules from the bulk to the liquid–liquid interface, and/or the particles displace the surfactant molecules from the interface to the bulk phase. Hence, the nanoparticles hinder the efficiency of TX-100 in reducing IFT.

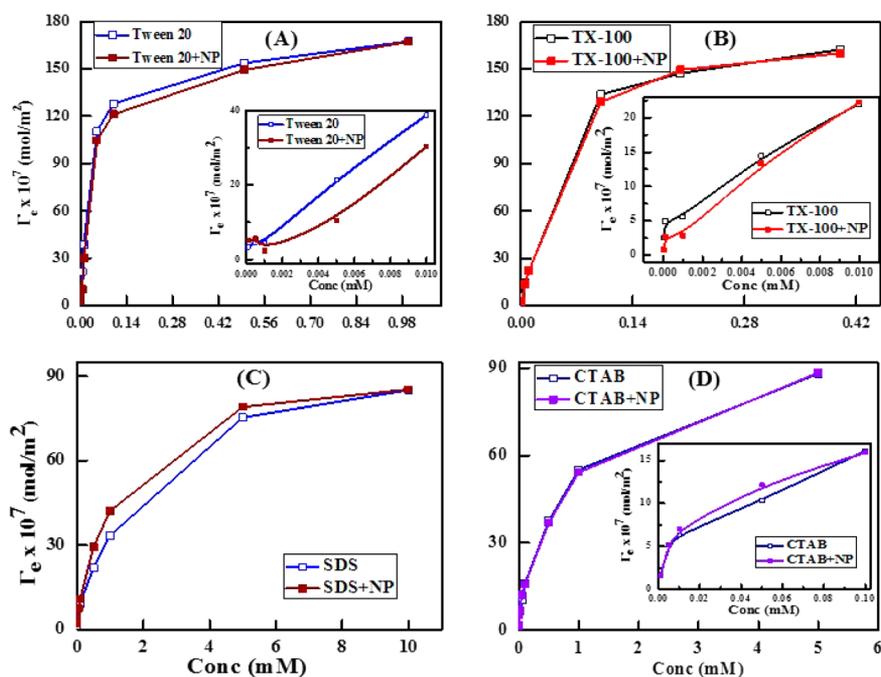
**3.2.1. Effect of Surface Excess Concentration of Different Surfactants in the Absence and Presence of NPs.** To quantify the effect of nanoparticle on the transportation of surfactant molecules from the bulk phase to the interface in the presence of nanoparticles, we have calculated the surface excess concentration of surfactant molecules as a function of concentration using the Gibbs equation:

$$\Gamma_e = -\frac{1}{nRT} \frac{\partial \gamma}{\partial \ln C} \quad (1)$$

where  $\Gamma_e$  is the surface excess concentration of surfactant,  $\gamma$  is the surface tension (mN/m),  $C$  is the bulk concentration (mM),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ), and  $T$  is the temperature (K), where  $n$  is the number of the solute species (respective surfactants) whose concentration at the interface changes with change in the bulk concentration  $C$ .

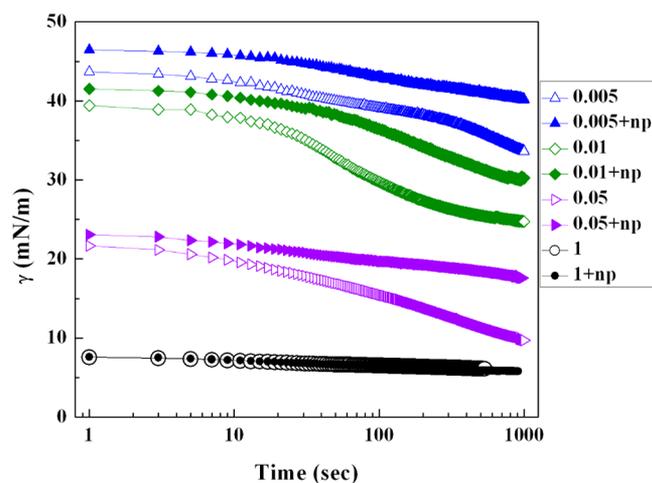
Panels A and B of Figure 2 present the surface excess concentration of different systems. It is evident from the figure that for both Tween 20 and TX-100 surfactants the surface excess concentrations of surfactant molecules at the *n*-hexane–water interface are lower in the presence of nanoparticles compared to those in the nanoparticle-free system. This is clearly visible at an intermediate concentration range, which is in a good agreement with the IFT data. Hence, it is apparent that the silica nanoparticles block the transportation of nonionic surfactant molecules from the bulk to the interface by adsorbing the surfactant molecules on its surface. This reduces the excess amount of surfactant molecules at the interface, leading to the reduction in the efficiency of surfactant to reduce the IFT. Thus, IFT increases in the presence of silica particles for nonionic surfactant in oil–water system. This behavior is in contrast to that seen for both ionic surfactants, SDS and CTAB, in the presence of nanoparticles, as shown in Figure 2C and 2D, respectively, where the surface excess concentration of surfactant molecules at interface are more than the pure system. Thus, in the case of ionic surfactants, nanoparticles clearly enhance the concentration of surfactant at the interface.

**3.3. Effect of Silica Nanoparticles on Dynamic Interfacial Tension of Different Surfactants.** Now we turn our attention to understand the dynamic IFT of the *n*-hexane–water system with different surfactants in the absence and presence of negatively charged silica NPs.



**Figure 2.** Surface excess concentration of Tween 20 (A), TX-100 (B), SDS (C), and CTAB (D) surfactants in the absence (open) and presence (solid) of silica nanoparticles. Insets present the data at low concentrations.

**3.3.1. Effect of Silica Nanoparticles on Dynamic Interfacial Tension of Tween 20 Surfactant Solutions.** The effect of 0.1 wt % nanoparticle on dynamic interfacial tension of Tween 20 surfactants at the *n*-hexane–water interface is presented in Figure 3.



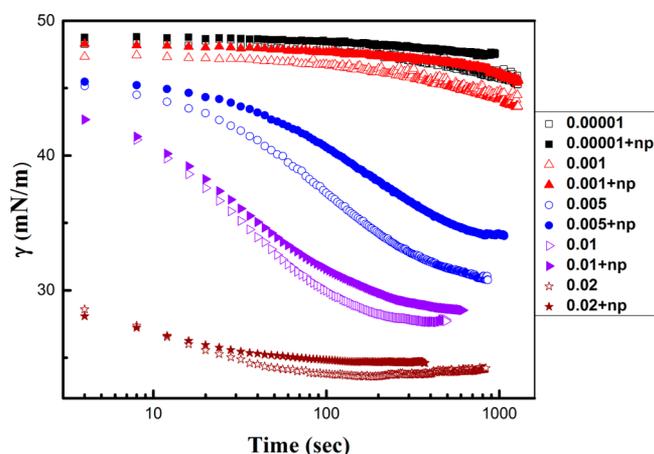
**Figure 3.** Interfacial tension at different concentrations (mM) of Tween 20 surfactants in the absence (open) and presence (solid) of 0.1 wt % silica nanoparticles at the *n*-hexane–water interface. Standard deviations are less than 1%.

It is evident from Figure 3 that in the case of pure Tween 20, with the increase in surfactant concentration, significant reduction in the initial as well as final interfacial tension occurs at the *n*-hexane–water interface, which is due to the increased number of surfactant molecules at the interface. However, an addition of 0.1 wt % silica nanoparticles to the surfactant solution enhances the IFT similar to the result obtained by Pichot et al.<sup>29</sup> The amount of increase in the IFT depends on the concentration of the surfactant solution. At a lower

concentration (0.005 mM), the IFT initially jumps to a higher value by a few mN/m. The difference from the pure surfactant case does not change much over time. On the contrary, the behavior is sensitive to the concentration of the surfactant. With an increase in the concentration to 0.01 mM, the difference in the dynamic interfacial tension is more at an intermediate period of time. Moreover, the rate of decrease in the dynamic surface tension is lower in the presence of NPs. However, the effect of nanoparticles diminishes with further increase in the concentration of surfactant, as clearly seen for the case of 1 mM.

**3.3.2. Effect of Silica Nanoparticles on Interfacial Tension of TX-100 Surfactant Solutions.** To verify the retarding effect on IFT, observed by Tween 20, a nonionic surfactant, is a generic behavior of all the nonionic surfactants at the *n*-hexane–water interface, we have conducted experiments using another nonionic surfactant TX-100 at the *n*-hexane–water interface in the absence and presence of NPs. The effect of 0.1 wt % nanoparticle on interfacial tension of TX-100 surfactants at the *n*-hexane–water interface is presented in Figure 4.

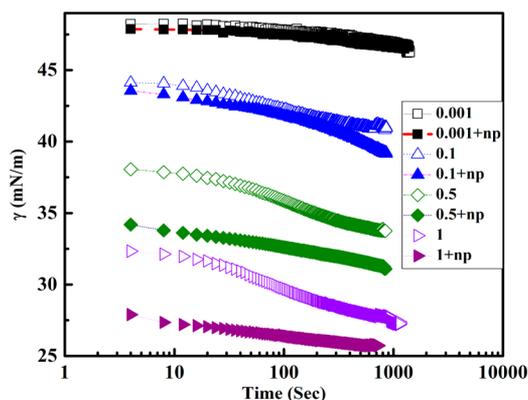
Figure 4 illustrates that at a very low pure TX-100 concentration, initial change in the dynamic interfacial tension value is not significant, in the presence of 0.1 wt % nanoparticles. This is observed for all the concentration of surfactant. As observed for the case of Tween 20, the dynamic surface tension decreases with time. However, silica nanoparticles retard the decreasing nature of the dynamical interfacial tension, leading to higher interfacial tension values compared to that seen without the nanoparticles. The effect of 0.1 wt % of silica NPs is most prominent at an intermediate range of surfactant (0.005 mM), analogous to that seen for Tween 20. A further increase in the surfactant concentration diminishes the effect of silica NPs, which is akin to the behavior seen for the Tween 20 case. The above results indicate that, similar to the Tween 20 behavior, addition of a nanoparticle on the nonionic surfactant, TX-100, hinders the transportation of



**Figure 4.** Interfacial tension at different concentrations (mM) of TX-100 surfactants in the absence (open) and presence (solid) of 0.1 wt % silica nanoparticles at the *n*-hexane–water interface. Standard deviations are less than 1%.

the TX-100 surfactant from bulk to interface. Consequently, fewer nonionic surfactant molecules move to the interface, resulting in the increase in the IFT of the *n*-hexane–water system.

**3.3.3. Effect of Silica Nanoparticles on Interfacial Tension of SDS Surfactant Solutions.** Although silica nanoparticles hinder the transportation of nonionic surfactants, do other kinds of surfactant behave similarly in the presence of silica NPs? To address the question, we have performed the experiment taking an anionic surfactant SDS with the *n*-hexane–water system. Figure 5 presents the results of the effect of 0.1 wt % silica nanoparticle on the interfacial tension of anionic SDS surfactants at the *n*-hexane–water interface.



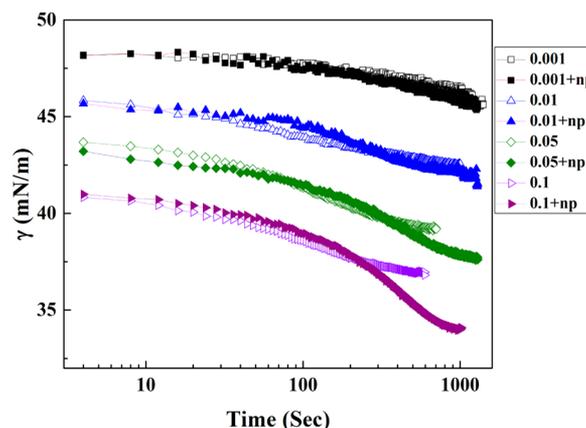
**Figure 5.** Interfacial tension at different concentrations (mM) of SDS surfactants in the absence (open) and presence (solid) of 0.1 wt % silica nanoparticles at the *n*-hexane–water interface. Standard deviations are less than 1%.

The behavior of the dynamic interfacial tension with time is similar to that seen for other cases. However, the relative behavior in the presence of NPs is strikingly different from that of nonionic surfactant. At a low concentration of surfactant, NPs do not affect the nature of IFT. However, with an increase in surfactant concentration, the effect of NPs is visible. Instead of an increase in the surface tension as seen for the nonionic surfactant case, we observe NPs facilitate surfactant adsorption at the interface. Thus, at a sufficient concentration of SDS,

there is a drop in the surface tension value. However, with time the difference among the two (with and without NPs) slightly reduces. It is expected that a further increase in the surfactant concentration will diminish the effect of NPs, as seen for other cases. However, the reduction in the IFT value in the presence of NPs for SDS is contrary to that seen for nonionic surfactants.

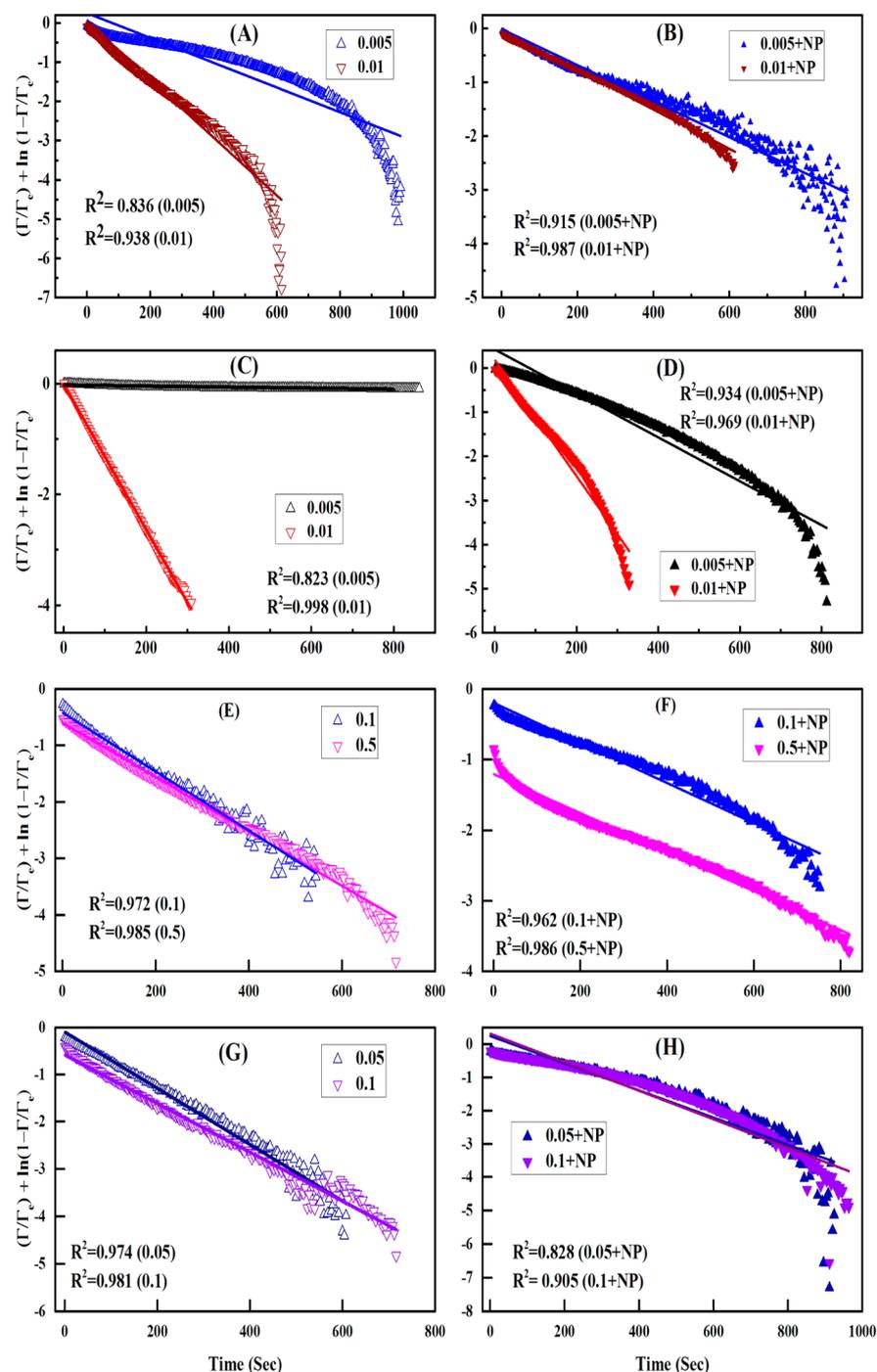
This can be explained as, in the case of anionic surfactant SDS, surfactant molecules are adsorbed at the *n*-hexane–water interface, which reduces the IFT. However, when negatively charged silica nanoparticles are introduced to the surfactant medium, due to the columbic repulsive interaction between negative charged surfactant molecule and negative charge silica NPs, NP forces more SDS surfactant molecules to go to the interface, further reducing the IFT. This indicates addition of NPs further facilitates more reduction in the interfacial tension at the *n*-hexane–water interface.<sup>16,33</sup> This is further supported by the surface excess concentration behavior discussed in section 3.2.1.

**3.3.4. Effect of Silica Nanoparticles on Interfacial Tension of CTAB Surfactant Solutions.** In the previous section, we investigated the effect of silica NPs on the IFT of the *n*-hexane–water system in the presence of an anionic surfactant. To complete the understanding on the effect of NPs on IFT in the presence of ionic surfactant, we extend our investigation for a system with cationic surfactant. The effect of 0.1 wt % silica nanoparticle on interfacial tension of cationic CTAB surfactants at the *n*-hexane–water interface is presented in Figure 6.



**Figure 6.** Interfacial tension at different concentrations (mM) of CTAB surfactants in the absence (open) and presence (solid) of 0.1 wt % silica nanoparticles at the *n*-hexane–water interface. Standard deviations are less than 1%.

The behavior seen for CTAB surfactant is similar to that of anionic surfactant; i.e., the NPs have a tendency to further reduce the interfacial tension of the system with CTAB surfactant. However, the effect of NPs is delayed such that the effect is visible only after 100 s even at 0.1 mM surfactant concentration. The effect of NPs is visible at an intermediate range of surfactant concentration akin to that seen for the SDS case, though the extent of reduction in interfacial tension is less than that observed for anionic SDS. Although the behavior of the CTAB system is similar to that of SDS, the reason for the reduction of the interfacial tension may be different. The presence of negatively charged silica nanoparticles in the positively charged CTAB surfactant medium causes electrostatic attraction among surfactant molecules and NPs. Subsequently, the surfaces of the silica nanoparticle are covered



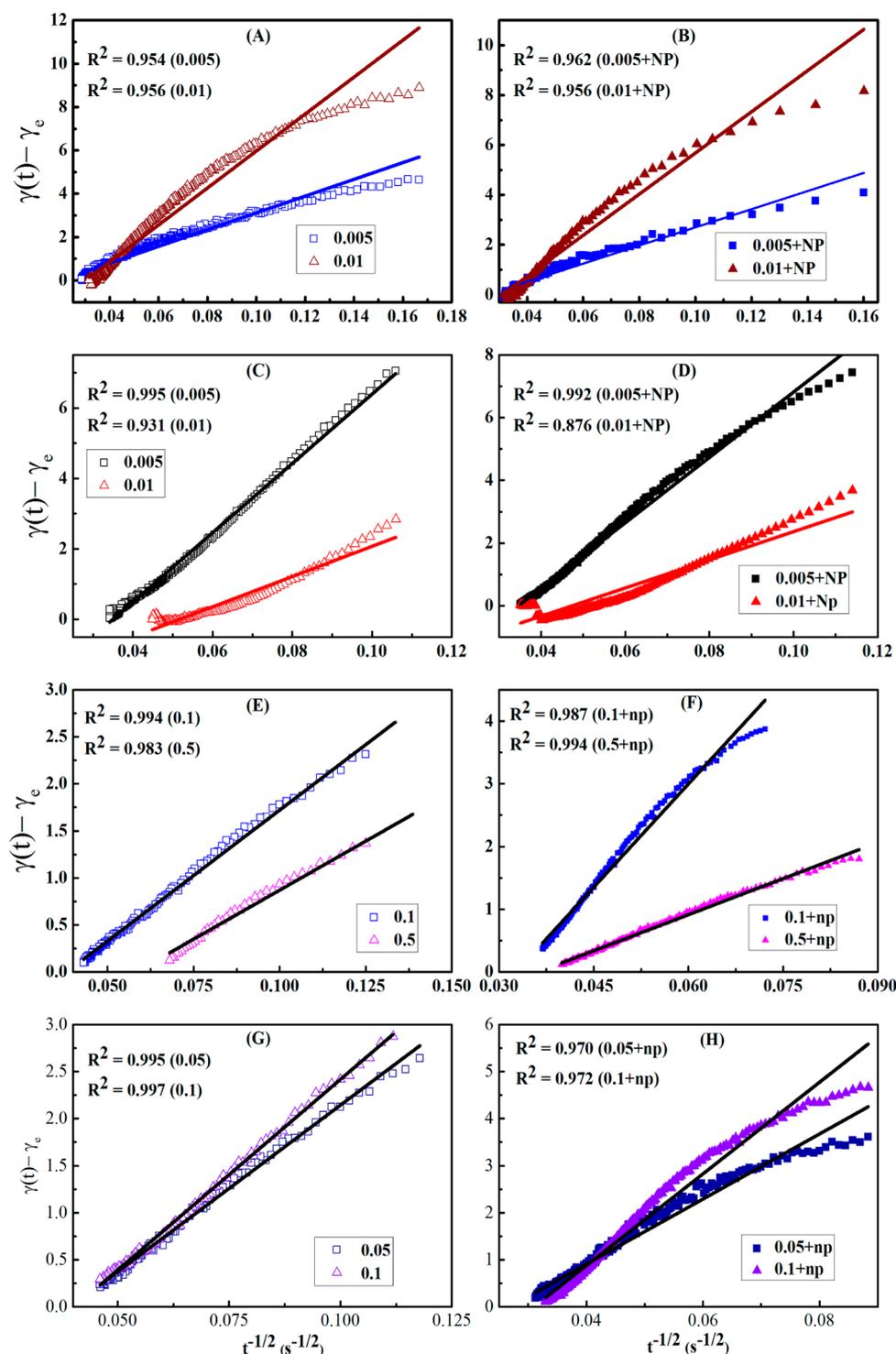
**Figure 7.** Dynamic surface excess concentration with time for SRT model at different concentrations (A) and (B) for Tween 20, (C) and (D) for TX-100, (E) and (F) for SDS, and (G) and (H) for CTAB, in the absence and in the presence of 0.1 wt % silica nanoparticles, respectively. Open symbols are for only surfactants, and solid symbols are for surfactants with nanoparticles. Up and down triangles are used for two different concentrations.

by surfactant molecules, resulting in the formation of hydrophobic nanoparticles. Thus, the modified NPs try to remain at the *n*-hexane–water interface, due to its hydrophobicity, which further decreases the interfacial tension.<sup>32,38</sup> The delay in the reduction of the interfacial tension is attributed to the reorganization of the NP–surfactant system.

**3.4. Diffusion and Adsorption Mechanism of Nanoparticles.** To understand the effect of a nanoparticle on the transportation mechanism of the surfactant from the bulk to the interface, the dynamic surface excess concentrations were

calculated from the dynamic interfacial tension data and fitted with two different models, viz., statistical rate theory (SRT) and the mixed diffusion kinetic controlled (DKC) model. The SRT model assumes that the adsorption is the rate-controlling step and the DKC model assumes the migration rate of surfactant to the interface is controlled by both diffusion and adsorption mechanisms.

The relation between surface excess concentration of surfactant and time when the system is close to equilibrium



**Figure 8.** Plot of  $\gamma(t) - \gamma_e$  in mN/m vs  $t^{-1/2}$  for DKC model close to equilibrium data, (A) and (B) for Tween 20, (C) and (D) for TX-100, (E) and (F) for SDS, and (G) and (H) for CTAB, in the absence and in the presence of 0.1 wt % silica nanoparticles, respectively. Open symbols are for only surfactants, and solid symbols are for surfactants with nanoparticles. Squares and triangles are used for two different concentrations.

on the basis of the SRT model as given by Ward et al.<sup>39</sup> and later modified by Azizian<sup>40</sup> is given by

$$\frac{\Gamma}{\Gamma_e} + \ln\left(1 - \frac{\Gamma}{\Gamma_e}\right) = \beta - \kappa t \quad (2)$$

where  $\beta$  and  $\kappa$  are constants and  $\Gamma$  and  $\Gamma_e$  are the dynamic surface excess concentrations at different time period and equilibrium time, respectively.

Figure 7 presents the plot of  $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$  as a function of time for four different surfactants, as studied in this work, in the absence and presence of 0.1 wt % silica nanoparticles.

In addition to the SRT model, we have also employed a mixed diffusion kinetic controlled (DKC) model where the migration rate of surfactant to the interface is controlled by both diffusion and adsorption mechanisms as described by

Table 2. Apparent Diffusion Coefficients,  $D_a$ , and Adsorption Rate Constants,  $k$ , for the SRT Model for Different Surfactants

surfactant	concentration (mM)	$D_a$ ( $10^9$ ) ( $m^2 s^{-1}$ )		adsorption rate constant, $k$ ( $s^{-1}$ ), for SRT model	
		absence of NPs	presence of NPs	absence of NPs ( $10^4$ )	presence of NPs ( $10^4$ )
Tween 20	0.005	303806	831	14	33
	0.01	1650619	1365	43	69
TX-100	0.005	586667	1161	0.9	50
	0.01	1426181	10160	151	146
SDS	0.1	90.66	3	52	28
	0.5	15	30	48	28
CTAB	0.05	231	6	60	42
	0.1	208	5	54	42

Ward and Tordai<sup>41</sup> and modified by Azizian et al.<sup>42</sup> The model is described below,

$$\gamma(t)_{t \rightarrow \infty} - \gamma_e = \frac{RT\Gamma_e^2}{2C_0} \left( \frac{\pi}{f(t)^2 D_a t} \right)^{1/2} \quad (3)$$

where  $f(t)$  is defined by

$$f(t) = \frac{\frac{\Gamma_e}{\Gamma_{sat}} \left( 1 - \frac{\Gamma_e}{\Gamma_{sat}} \right)}{\frac{\Gamma}{\Gamma_{sat}} \left( 1 - \frac{\Gamma}{\Gamma_{sat}} \right)} \quad (4)$$

where  $\gamma(t)$  is the dynamic interfacial tension,  $C_0$  is the bulk concentration of surfactant,  $\Gamma_{sat}$  is the saturated dynamic surface excess concentration,  $\pi$  is the surface pressure, and  $D_a$  is the apparent diffusion coefficient.

In the mixed diffusion kinetic controlled model, the plot of  $\gamma(t) - \gamma_e$  vs  $t^{-1/2}$  should be linear. Figure 8 presents the interfacial data and the corresponding fit as per the DKC model for the four surfactants with different concentrations in the absence and presence of silica nanoparticle.

The fit of the data as shown in Figures 7 and 8, using two different models, indicates relatively better performance of the DKC model. Thus, in general, the migration rate of surfactant and nanoparticles to the interface are controlled by both diffusion and adsorption mechanisms.

The apparent diffusion coefficients,  $D_a$ , for all systems are calculated using eq 4 and the slope of plot  $\gamma(t) - \gamma_e$  vs  $t^{-1/2}$  and are summarized in Table 2. Table 2 also includes the adsorption rate constant evaluated using the SRT model.

Table 2 suggests two distinct behaviors of the apparent diffusion coefficient for all four surfactants. In the case of both nonionic surfactants,  $D_a$  increases with an increase in surfactant concentration. On the contrary, for both ionic surfactants,  $D_a$  decreases with increasing surfactant concentration. For the case of the nonionic system, increasing the concentration of surfactant increases the  $D_a$ , leading to a higher adsorption rate. This is also supported by the enhanced adsorption rate,  $k$ , value of the SRT model. In comparison to nonionic surfactants, the behavior for both ionic surfactants, SDS and CTAB, are found to be different. In the case of SDS and CTAB, the  $D_a$  decreases with an increase in surfactant concentration, which perhaps may be due to electrostatic repulsion among surfactant molecules in the process of transportation from the bulk to the interface, which slows down the rate of adsorption.

The presence of negatively charged silica nanoparticle affects the behavior of surfactants, depending on the nature of surfactants. In the case of the nonionic surfactants,  $D_a$  increases with the increasing the concentration of surfactant, in the

presence of NPs, with a higher rate of adsorption, which is also justified by the values of  $k$  (Table 2).

On the contrary, we observed two different results for ionic surfactants. In the case of anionic SDS surfactant,  $D_a$  values increases with an increase in concentration, in the presence of negatively charged silica nanoparticles. This may be due to the repulsive interaction among nanoparticles and surfactants, which forces additional surfactant molecules to the interface, leading to a higher adsorption rate. On the contrary, in the case of cationic surfactant, CTAB,  $D_a$  slightly decreases with an increase in surfactant concentration, which may be due to electrostatic attraction among the positive charge CTAB and negative charged silica nanoparticle. However, the effect is not as dramatic as seen for other cases, which is reflected in the negligible change in the overall rate of adsorption constant. To provide molecular insight into the above phenomena of surfactants nature in the presence of nanoparticles, we have initiated a molecular simulation study, the results of which will be reported elsewhere.

## CONCLUSIONS

In this study, we have compared the effect of negatively charged silica nanoparticles on the interfacial tension of the *n*-hexane–water system using different surfactants such as Triton X-100, Tween 20, SDS, and CTAB. Outcomes of the study are summarized as follows:

1. Inclusion of negatively charged silica NPs enhances the performances of SDS and CTAB in further reduction of the interfacial tension. On the contrary, in the case of nonionic surfactant, Tween 20 and TX-100, the same silica NPs increase the interfacial tension to a further extent.
2. Calculation of surface excess concentration of different surfactants in the absence and presence of NPs clearly depicts that for ionic surfactants, SDS and CTAB, surface excess concentration of surfactants at the interface increases in the presence of NPs. On the contrary, in the case of nonionic Tween 20 and TX-100, NPs decrease the surface excess concentration of surfactants.
3. The dynamic interfacial tension data were fitted with two different dynamic models, diffusion kinetic control (DKC) and statistical rate theory (SRT) and found that the diffusion kinetic control model represents the system more accurately.
4. The mechanism of surfactant adsorption at the interface in the absence and presence of NPs is well supported by the apparent diffusion coefficients calculations for all the surfactant systems.

## ■ AUTHOR INFORMATION

## Corresponding Author

\*J. K. Singh. Contact number: (0512) 2596141. Fax: (0512) 2590104, 2590007. E-mail: jayantks@iitk.ac.in.

## Notes

The authors declare no competing financial interest.

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