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PAPER

Interfacial behavior of nonionic Tween 20 surfactant at oil–water interfaces in the presence of different types of nanoparticles

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In this paper, we have studied the effect of three different types of nanoparticles (NPs) (e.g. SiO_2, TiO_2, and ZnO) on the interfacial tension (IFT) of different oil–water systems (e.g. oil: n-hexane, n-heptane, n-decane, toluene). The IFT of different oil–water systems, at variable concentrations of a nonionic surfactant, Tween 20, in the absence and presence of three different NPs was examined. As expected, the presence of Tween 20 surfactant effectively reduces the initial as well as final IFT of the n-hexane–water system. However, inclusion of NPs, irrespective of charge, alters the efficacy of Tween 20 surfactant in further reducing the IFT. In order to investigate the retarding efficiency of NPs on Tween 20 surfactant, the surface excess concentration of surfactants in the presence of 0.1 weight% of different NPs was also inspected along with apparent diffusion coefficients (D_a). It has been found that the surface excess of surfactants at the interface decreases in the presence of NPs. Also increasing the concentration of Tween 20 surfactant increases the D_a, leading to a higher adsorption rate. However, similar to a surface excess of surfactant, D_a values are less in the presence of NPs compared to the particle free system.

1. Introduction

Emulsions have great practical importance in numerous applications, including foodstuffs, cosmetics, painting, printing,[1,2] pharmaceutical industries,[3] enhanced oil recovery,[4,5] oil-spill remediation[6] etc. The emulsion can be stabilized by addition of surfactants, amphiphilic polymers,[7–9] proteins or other large biological macromolecules.[10,11] These molecules lower the energy required for droplet formation and also provide a steric/ electrostatic barrier against droplet coalescence.

Addition of nanoparticles at liquid–liquid interfaces can also be used for the stabilization of emulsions. Adsorbed nanoparticles at interfaces, lowers the free energy of the system by reducing the surface area of contact between interfaces.[12–14] Nanoparticle stabilized emulsions have advantages over hazardous and toxic surfactant stabilized emulsions. Particle stabilized emulsions can be utilized for the production of macroporous materials used as bioscaffolds, low-weight structures,[9,15] solid-coated capsules, encapsulation of chemicals, drugs etc.[16–18]

There are numerous studies available on the effect of NPs on interfacial tension (IFT) of liquid–liquid system.[11,19–22] Vignati and Piazza[11] compared the effect of surface-untreated silica nanoparticles to that of hexamethyldisilazane treated silica on the IFT of an isooctane or octanol oil droplet in water. They discovered that IFT did not change with the variation of either the nanoparticle concentration or the hydrophobicity of their

surface. Saleh et al.[19] reported that bare silica nanoparticles do not affect the IFT of trichloroethylene–water and heptane–water systems. However, highly charged poly(styrenesulfonate)-grafted silica particles was found to reduce oil–water IFT significantly. Pichot et al.[20] also reported that presence of the hydrophilic silica particles at vegetable oil–water interface has no effect on IFT. Moghadam and Azizian[21] examined the IFT of ZnO nanoparticles at n-decane–water interface, and observed that nanoparticles on their own are unable to reduce the IFT, which is similar to the results obtained by Moghadam et al.[22] On the other hand, merely nanoparticles are sometimes found to be surface inactive.

In view of the widespread applications of emulsions relevant to a range of industrial applications such as processing of minerals, membrane-based separation, purification, cleaning and detergency, many researchers have studied the stability of emulsions in presence of nanoparticles by different types of cationics,[21–26] anionics,[27–30] and by both the cationic and anionic surfactants.[31,32] However applications like cosmetics and personal care, food products, pharmaceuticals, etc., nonionic surfactants[14,20,28,32,33] are used with nanoparticles to stabilize the emulsions.

Ravera et al.[23] investigated the silica colloidal dispersions at hexane–water interface in presence of different amount of cationic surfactant, cetyltrimethyl ammonium bromide, (CTAB) in order to tune the hydrophobicity of the particles and their effect on the interfacial properties. Similar to Ravera et al. the IFT at dodecane–water and light paraffin liquid–water in presence of both silica nanoparticles and cationic surfactant, CTAB, has also been investigated by Binks et al.[24] and Lan et al.[25]

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respectively. In addition, Moghadam and Azizian,[21] studied the effect of ZnO nanoparticle on the IFT of decane–water system in presence of cationic surfactant CTAB.

The effect of anionic surfactant, sodium dodecyl sulfate (SDS), at n-dodecane–water system using positively charged silica particles has been investigated and found synergistic stabilization of oil–water emulsions by Binks and Rodrigues.[27] Ma et al.[28] investigated trichloroethylene (TCE)–water IFT with an emphasis on systems containing both anionic surfactants, SDS and negatively charged hydrophilic silica nanoparticles. They observed that silica nanoparticles increases the efficiency of the SDS surfactants in reducing the IFT because the repulsive interactions between the SDS surfactant and nanoparticles promote more number of surfactants to adsorb at TCE–water interface thus reducing IFT further. Similar kinds of results are obtained for n-decane–water system containing SDS and ZnO nanoparticle by Moghadam and Azizian.[21] Where the presence of ZnO nanoparticles makes the SDS molecules more efficient to decrease the IFT. Saien et al.[30] investigated the influence of SDS and magnetite nanoparticles on IFT of n-hexane–water system and found that introducing NPs into SDS solutions caused the IFT reduction to intensify.

A reduction in the IFT of hexadecane–water system in the presence of cationic surfactant, dodecylamine (DDA), or anionic surfactants, palmitic acid (PA), was found to occur with addition of charged colloidal particles such as: kaolin, alumina, silica in the aqueous phase as investigated by Wang et al.[31] IFT of ZrO_2 nanoparticles at n-heptane–water system in presence of anionic surfactant, SDS and cationic surfactant: dodecyl trimethyl ammonium bromide ($C_{12}TAB$) has been investigated by Esmaeilzadeh et al.[32] and found that IFT also decreases.

Ma et al.[28] investigated effect of non-ionic surfactants, Triton X-100 and tetraethylene glycol alkyl ethers $C_{12}E_4$ and $C_{14}E_4$, on trichloroethylene (TCE)–water IFT in presence of negatively charged hydrophilic silica nanoparticles. They observed that, $C_{12}E_4$ and $C_{14}E_4$ molecules, with or without the presence of nanoparticles, fail to decrease the TCE–water IFT. However Triton X-100 surfactants effectively decrease the IFT, but inclusion of nanoparticles does not influence Triton X-100 efficiency. Esmaeilzadeha et al.[32] studied the reduction of IFT of ZrO_2 nanoparticles at n-heptane–water system in presence nonionic surfactant (lauryl alcohol 7 mole ethoxylate, LA7) and found that the nanoparticle has negligible effect on the interfacial behavior in this system. Pichot et al.[20] studied the effect of hydrophilic silica particles and Tween 60 surfactant at the vegetable oil–water interface. They found that at a low surfactant concentration, the IFT become higher compared to particle-free systems. On the other hand, the nanoparticles were found to have no effect at a high surfactant concentration.

From the above discussion we observed that solely nanoparticle are found to be surface inactive in terms of reducing IFT, however when these nanoparticles are added with cationic or anionic surfactants, it increases the efficiency of surfactants irrespective of charges, in reducing the IFT compared to particle free system. Despite the significant works on IFT based on the survey it is found that, most of the studies till date mainly considered one particular type of nanoparticle or/and one particular surfactant at a fix oil–water system. However, there is

a lack of information in literature on the effect of different types of NPs with respect to zeta (ζ) potential in different oil–water systems, with increase in chain length as well as aliphatic to aromatic with variation in volume fraction in absence and presence of surfactant. Hence, the aim of the present work is to study the effect of three different types of nanoparticles (NPs) (e.g. SiO_2, TiO_2, and ZnO) on the interfacial tension (IFT) of different oil–water systems (e.g. oil: n-hexane, n-heptane, n-decane, toluene) with variation in weight%. Further, in this work, we aim to investigate the IFT at variable concentrations of one nonionic surfactant: Tween 20, in absence and presence of all these three different types of NPs.

2. Material and method

2.1 Materials

Three different types of NPs viz., SiO_2, TiO_2 and ZnO were used in this work. The SiO_2 NPs was purchased from Otto chemicals Pvt. Ltd., Mumbai, India. TiO_2 and ZnO were purchased from DS scientific and Nano Technology, Mumbai, India. The nonionic surfactant Tween 20 (99% purity) was purchased from Loba Chemicals Pvt. Ltd. Mumbai, India. The n-hexane (Rankem, Gujarat, India), n-heptane (Loba Chemicals Pvt. Ltd, Mumbai, India), n-decane (Sd fine chemicals Ltd, Mumbai, India), and toluene (Fisher Scientific, Mumbai, India) of 99% purity were used as oil phase. The zeta potential of three different types of nanoparticles were measured by Zetasizer Nano ZS (Malvern, U.K.) and found to be −23.63, −5.56 and 17.8 mV for SiO_2, TiO_2 and ZnO, respectively.

Aqueous solutions of surfactant was made by ultrapure water (Millipore India Private Limited, India) of 18.2 MΩ cm resistivity, 71.5 mN m^{-1} surface tension, and 6.5–7 pH at 25 °C. For all the experiments a surfactant solution of desired concentration was prepared by diluting a concentrated stock solution.

2.2 Methods

2.2.1 Pendant drop tensiometry (PDT). The IFT of different concentrations of surfactant without and with different weight (wt)% of different nanoparticles at oil–water system were measured at 25 °C by the pendant drop technique using Goniometer (OCA 35, Data physics, Germany). A 50 μL volume drop of different concentration of surfactant solutions without and with NPs were produced at the tip of a stainless steel needle (outer diameter 1.65 mm) immersed in a bulk oil phase. The shape of the drop was captured by a high-speed camera and image profile was fitted with Young–Laplace equation to obtain the IFT (γ). The software of the OCA 35 is well equipped to use the image profiles captured by the camera to produce IFT (dynamic IFT) as a function of time. All the experiments are repeated three times and average values are reported.

2.2.2 Nanofluid preparation. For the preparation of nanofluid, 0.1 wt% of different nanoparticles were added to different concentration 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.
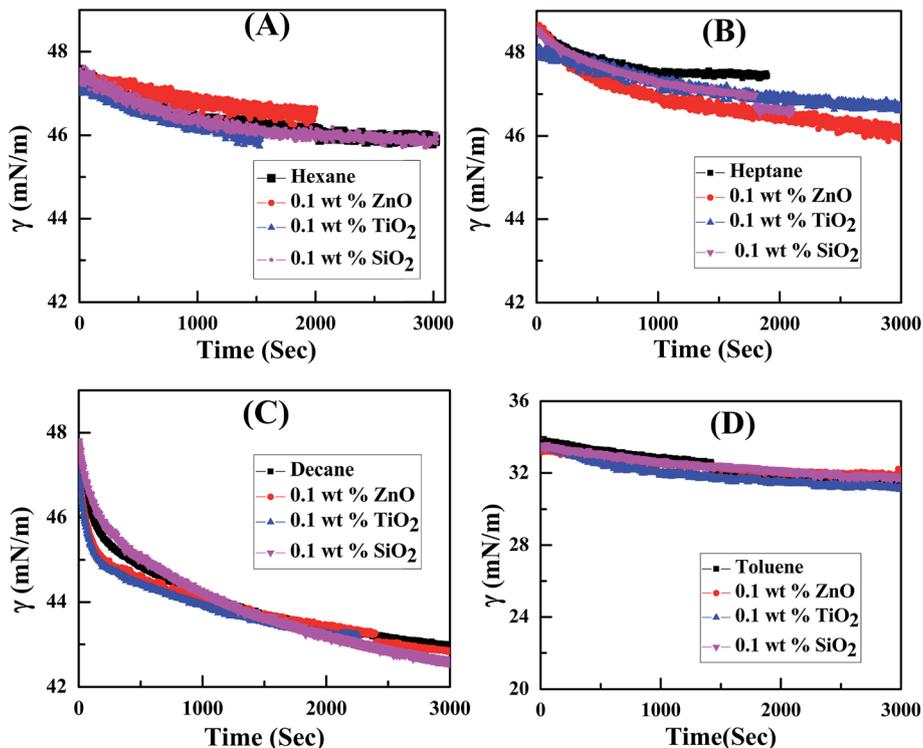
Fig. 1 IFT of different oil–water systems: (A) *n*-hexane, (B) *n*-decane, (C) *n*-heptane, (D) toluene, in absence and presence of 0.1 weight% of ZnO, TiO$_2$, and SiO$_2$ NPs. Standard deviations are less than 1%.

3. Results and discussion

3.1 Effect of three different types of NPs on dynamic IFT of different oil–water systems

The IFT of different oil–water systems such as *n*-hexane–water, *n*-heptane–water, *n*-decane–water, and toluene–water, was measured taking 0.1 weight% of different NPs: SiO$_2$, TiO$_2$, and ZnO for a long period of time (∼3000 second) and are presented in Fig. 1.

The IFT values of *n*-hexane–water, *n*-heptane–water, *n*-decane–water and toluene–water system are found to be 47.6, 48.99, 47.69, 48.94 and 33.60 mN m^{-1} respectively which are similar to the kind of results already reported in literatures.[20,21,23,34,35] The IFT of different oil–water system in presence of different NPs were measured for period of time and observed that IFT remains almost constant irrespective of charges of NPs. In other words, the solely NPs have no role in reducing the IFT value of different oil–water system.

Since we did not get any change in IFT of different oil–water interface even though addition of 0.1 weight% of different nanoparticle, in the next section we describe the effect of different weight% of nanoparticle considering *n*-hexane–water system.

3.2 Effect of weight% of different types of NPs on IFT of *n*-hexane–water system

The IFT of the NP free *n*-hexane–water system was first measured and found to be 47.6 mN m^{-1}, which is in excellent

agreement with the literature.[23,30,34,36] Subsequently the IFT of *n*-hexane–water system in the presence of three different NPs were measured over a long period of time and the results are presented in Fig. 2.

It is observed that with increase in the weight% of the three different types of NPs at *n*-hexane–water interface, the IFT remain almost constant for the same period of time. Hence, it is evident that the sole NPs have no role in reducing the IFT value of *n*-hexane–water system, which is similar to the result obtained by many researchers for different NPs.[20,21,23,28]
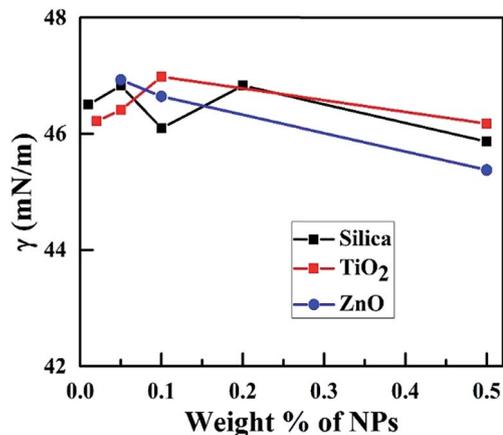
Fig. 2 Change in IFT with variation in weight% of different NPs at *n*-hexane–water interface (standard deviations are less than 1%).
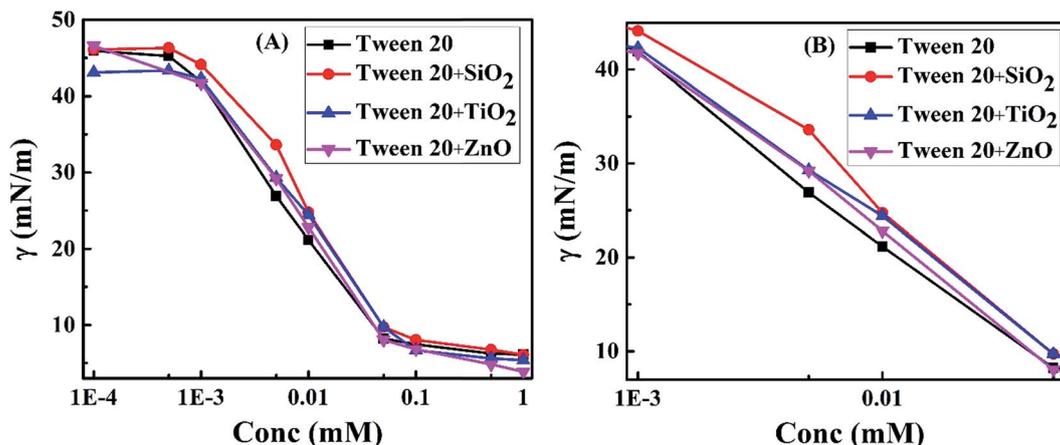
Fig. 3 (A) Equilibrium IFT of Tween 20 (■) surfactants in presence of 0.1 wt% different NPs: SiO$_2$ (●), TiO$_2$ (▲) and ZnO (▼) at *n*-hexane–water interface. (B) IFT data at concentration range of 0.001 to 0.05 mM (standard deviations are less than 1%).

Now, we turn our attention to examine the effect of mixture of different NPs with one nonionic surfactant on the interfacial behavior of *n*-hexane–water system.

3.3 Effect of three different types of NPs on equilibrium IFT of Tween 20 surfactant solution

The equilibrium IFT of a nonionic surfactant: Tween 20, at *n*-hexane–water system in presence of 0.1 weight% of different types of NPs: SiO$_2$, TiO$_2$ and ZnO, were compared with the NP free system over a long period of time (~3000 seconds) and are presented in Fig. 3(A) and (B).

Fig. 3 clearly demonstrates that the IFT of Tween 20 surfactants at *n*-hexane–water system decreases with the increase in concentration of the surfactants. However, the IFT value reaches a limiting value after CMC (CMC of Tween 20 = 0.05–0.08 mM), as expected. Similar to pure surfactant, in case of mixtures of surfactant and different types of NPs: SiO$_2$, TiO$_2$, and ZnO, the IFT also decreases with increase in surfactant concentration and no further reductions in IFT were observed after CMC.

However the IFT of Tween 20 surfactant rises in presence different NPs irrespective of charges, compared to the NP free *n*-hexane–water system. In other words IFT of Tween 20 surfactants in presence of NPs are more than that of NP free *n*-hexane–water system.

In case of mixtures, all the three NPs, irrespective of charges, retard the efficiency of Tween 20 surfactant in reducing IFT. This peculiar characteristic was earlier reported in our last work Biswal *et al.*[37] The increase in IFT in presence of NPs is mainly attributed the fact that the NPs hinders the transportation of the Tween 20 surfactant molecules from bulk to interface. Due to the affinity of surfactant molecules towards the NPs, the surfactant molecules adhere to the surface of NPs, and stay in the bulk phase leading to less availability of surfactant molecules to transport to the interface. Thus, due to the presence of relatively less free surfactant molecules at the interface, IFT increases in presence of NPs.

Now we turn our attention to understand the dynamic IFT of nonionic surfactants: Tween 20 at *n*-hexane–water system in absence and presence of different NPs.

3.4 Effect of three different types of NPs on dynamic IFT of Tween 20 surfactant solution

Fig. 4 presents the effect of different NPs on dynamic IFT of Tween 20 surfactant solutions.

It is clear from Fig. 4 that, for all the systems, at all surfactant concentrations in the absence and presence of NPs, the dynamic IFT of the Tween 20 surfactant at *n*-hexane–water system decreases with time. In contrast, there occurs an increase in IFT, by the addition of 0.1 weight% of NPs to the surfactant solution, which is similar to kind of results reported earlier by Pichot *et al.*[20]

In order to verify that the retarding effect of SiO$_2$ NPs on IFT of Tween 20, a nonionic surfactant, is a generic behavior for all the NPs at the *n*-hexane–water interface, experiments on IFT of Tween 20 surfactant, using two more NPs: TiO$_2$ and ZnO at the *n*-hexane–water interface were conducted. The effect of 0.1 weight% of SiO$_2$, TiO$_2$ and ZnO NPs on IFT of Tween 20 surfactants at *n*-hexane–water interface are presented in Fig. 4(A), (B) and (C) respectively.

As detected for SiO$_2$, ($\zeta = -23.63$ mV) similar kind of IFT results was also observed for TiO$_2$ ($\zeta = -5.56$ mV) and ZnO ($\zeta = 17.8$ mV) for Tween 20 surfactants at *n*-hexane–water interface. This indicates, irrespective of charges of NPs, IFT of Tween 20 surfactants-*n*-hexane–water system increases by the addition of 0.1 weight% of the NPs in the solution compared to NP free system. This may be attributed to the NPs ability to block the transportation of surfactant from bulk to interface. This would be evident from the changes in the surface excess concentration in the presence of NPs, which is described below.

3.5 Effect of surface excess concentration of different surfactants in the absence and presence of NPs

The surface excess concentration of surfactant in presence of nanoparticle and particle free system has been calculated to examine the retarding capacity of NPs in term of transportation of surfactant molecules from bulk to interface. The surface excess concentration of surfactant has been calculated using the Gibbs equation:
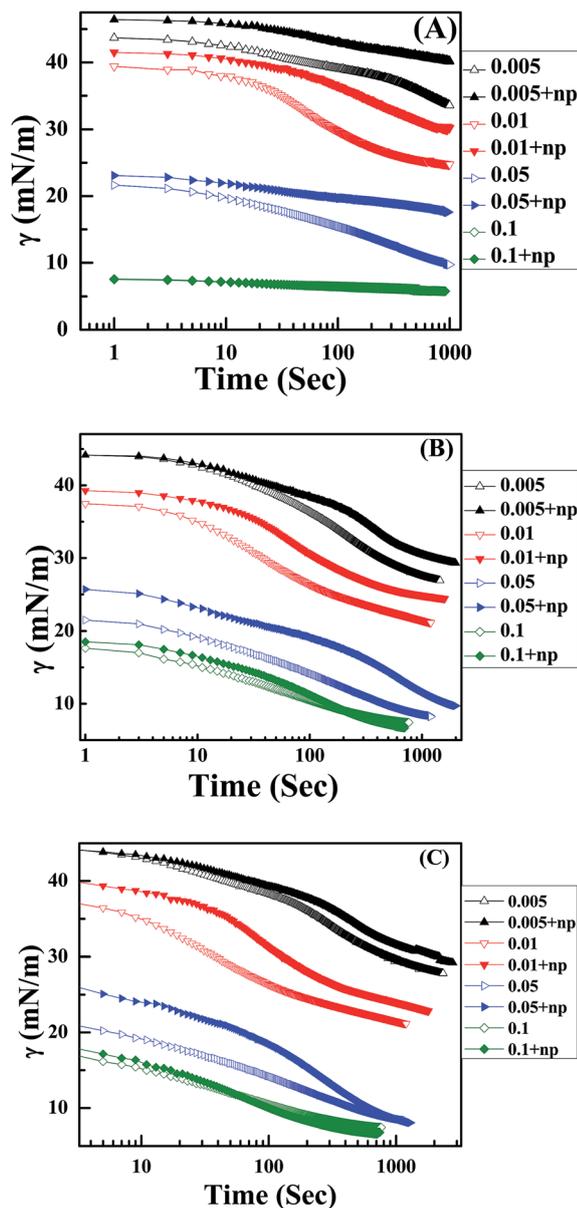
Fig. 4 IFT of Tween 20 surfactants in absence and presence of 0.1 weight% of different NPs (A) SiO_2, (B) TiO_2, and (C) ZnO at n-hexane–water interface (standard deviations are less than 1%).

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

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

The surface excess concentration of Tween 20 surfactants in absence and presence of different NPs are presented in Fig. 5 (A) SiO_2, (B) TiO_2 and (C) ZnO.

The surface excess concentration of Tween 20 surfactants, in presence or absence of NPs increases monotonously until it reaches an equilibrium value. It is clear from Fig. 5, that in

presence of NPs of different types $viz.$, SiO_2, TiO_2 and ZnO irrespective of its charge, the surface excess concentrations of Tween 20 surfactant at the n-hexane–water interface are lower than that of nanoparticle-free system. This indicates that the NP blocks the transportation of surfactant molecules from the bulk phase to the interface. Therefore, presence of NPs reduces the efficiency of surfactant to reduce the IFT. In other words, NPs increase the IFT of the Tween 20 surfactants-oil–water system. Since the surface excess concentration of surfactant at interface are less in presence of NPs compared to the corresponding particle free system, it suggests that the surfactant molecules are adsorbed on the surface of NPs and remain in bulk phase. This behavior is in contrast to that seen by different authors for all types of surfactants studied earlier in the presence of different NPs.

There are two possible mechanisms to explain the increase in IFT:

(a) NPs adsorb directly at the interface, and thus less number of surfactants gets adsorbed at the interface.

(b) The surfactant molecules get adsorb on the surface of NPs, and thus less number of free surfactants is available at the interface.

The deposition of nanoparticles at the interface, mechanism (a), can be one explanation why less Tween 20 molecules are present at the interface. However, we have examined with increasing weight% of NP, which does not alter the IFT. Thus, increase in IFT as observed for the current system due to mechanism (a) is not the best possible reason.

Therefore, we believe that the mechanism (b) is the main reason for the increase in IFT in the current work. This is well supported by a recent work of Bharti $et\ al.$,[38] which clearly demonstrate that non-ionic surfactants adsorb well on NPs. Increase in IFT due to adsorption of surfactant molecules on NPs is also reported by other authors.[20,23]

3.6 The kinetic model fittings: statistical rate theory (SRT) and diffusion kinetic controlled (DKC)

In order to understand the adsorption mechanism of surfactant both at the interface, on the NPs and transportation from bulk to interface, we have calculated the surface excess concentration of Tween 20 surfactant and fitted with two different kinetic models, $viz.$, statistical rate theory (SRT) and the mixed diffusion kinetic controlled (DKC).

The relation between surface excess concentration of surfactant and time when the system is close to equilibrium on the basis of the SRT model, as given by Ward $et\ al.$[39] and later modified by Azizian,[40] is given by

$$\frac{\Gamma}{\Gamma_e} + \ln\left(1 - \frac{\Gamma}{\Gamma_e}\right) = \beta - kt \qquad (2)$$

where β and k are constants and Γ and Γ_e are the dynamic surface excess concentrations at different time period and equilibrium time, respectively.

The slope of the plot of $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$ as a function of time (t) for all these systems for Tween 20 surfactant in presence of all these two types of NPs: TiO_2 and ZnO, studied in this work are presented in Table 1.
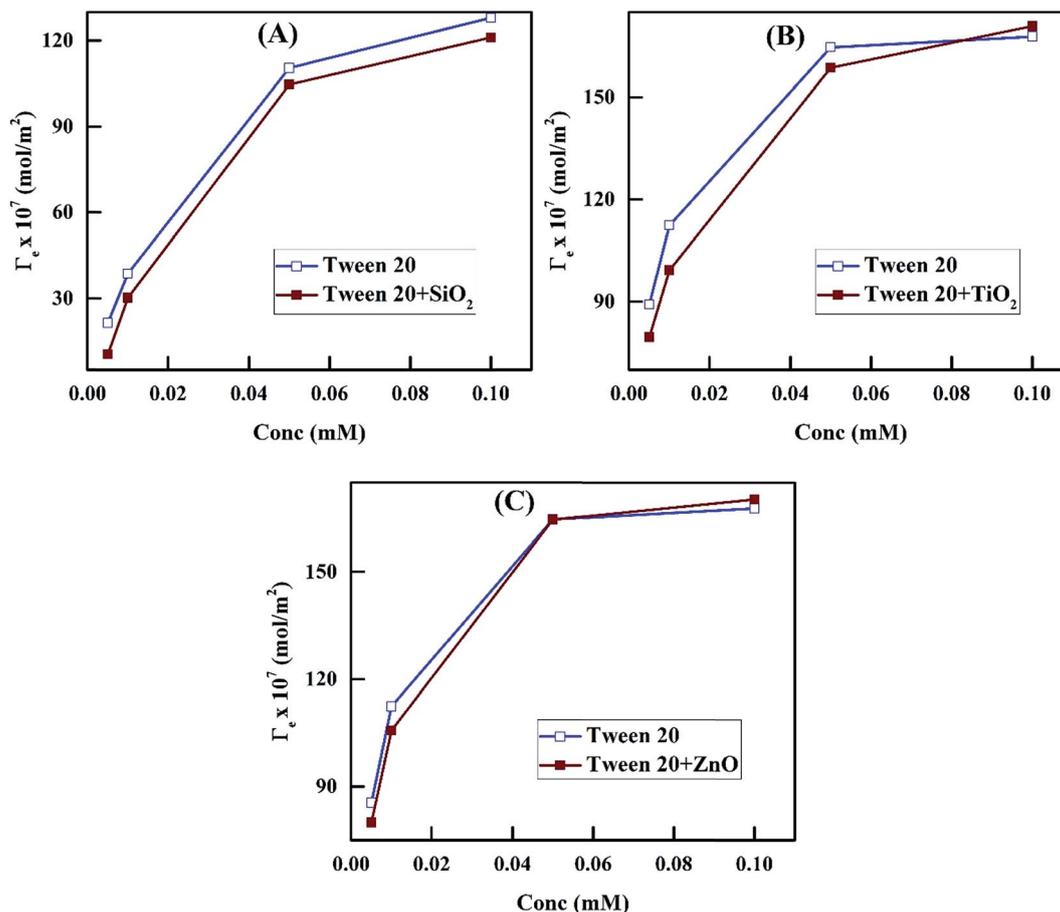
Fig. 5 Surface excess concentration of Tween 20 surfactants in absence (open) and presence (solid) of different NPs: SiO_2 (A), TiO_2 (B), and ZnO (C).

Table 1 Adsorption rate constants, k (s^{-1}) (10^4), for the SRT model calculated from the plot of $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$ vs. (t) for different NPs with R^2 values

Concentration (mM)	Tween 20		Tween 20 + TiO$_2$		Tween 20 + ZnO	
	k	R^2	k	R^2	k	R^2
0.005	27	0.992	19	0.995	10	0.986
0.01	30	0.968	26	0.986	20	0.963
0.05	31	0.996	18	0.981	31	0.994
0.1	57	0.993	55	0.997	73	0.994

In additional to the SRT model, we have employed 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 Ward and Tordai,[41] and modified by Azizian et al.[42] The model is described below,

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

where $f(t)$ is defined by

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

where $\gamma(t)$ is the dynamic IFT, C_0 is the bulk concentration of surfactant, Γ_{sat} is the saturated dynamic surface excess concentration, π 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. The apparent diffusion

Table 2 Apparent diffusion coefficients, D_a, (10^{11}) ($m^2 s^{-1}$) for DKC model calculated by the plot of $\gamma(t) - \gamma_e$ vs. $t^{-1/2}$ for different NPs along with R^2 values

Concentration (mM)	Tween 20		Tween 20 + TiO$_2$		Tween 20 + ZnO	
	D_a	R^2	D_a	R^2	D_a	R^2
0.005	37.245	0.905	8.616	0.936	9.040	0.890
0.01	159.675	0.989	19.998	0.990	13.676	0.992
0.05	188.791	0.906	21.630	0.961	14.825	0.892
0.1	241.002	0.973	23.588	0.940	28.789	0.982

coefficients, D_a, for Tween 20 surfactant in absence and presence of all these two types of NPs: TiO$_2$ and ZnO are calculated using the slope of the plot $\gamma(t) - \gamma_e$ *vs.* $t^{-1/2}$ and are summarized in Table 2.

The fit of the data using two different models, along with R^2 values are summarized in Tables 1 and 2. Table 1 indicates relatively better performance of the SRT model compare to DKC with respect to R^2 values. Thus, in general, adsorption can be concluded as a rate-controlling step.

Table 2 compares the apparent diffusion coefficient, D_a, as a function of surface concentration for systems containing Tween 20 only and Tween 20 with TiO$_2$ and ZnO NPs. Table 2 suggests that, D_a increases with an increase in Tween 20 surfactant concentration. For the case of Tween 20 surfactant, increasing the concentration of surfactant increases the D_a, leading to a higher adsorption rate. However D_a values are less, in presence of NPs: TiO$_2$ and ZnO, compared to particle free system. This suggests that the adsorption amount of the surfactant at the interface decreases in presence of NPs. This is similar to the kind of result reported for SiO$_2$ with Tween 20 surfactant in our earlier publication Biswal *et al.*[37]

Based on the above results, we can conclude the following: (a) NPs solely are unable to reduce the IFT, (b) NPs retard the efficiency of Tween 20 surfactant in reducing IFT of *n*-hexane–water system. Thus, it is now clear that NPs can affect the behavior of Tween 20 surfactant in *n*-hexane–water system. However, it is not clear if such effect is likely for different chain length of oils. To this end, we investigated the effect of different

oils on the nature of dynamic IFT of Tween 20-oil–water system in the presence of NPs, which is discussed below.

3.7 Effect of ZnO NPs on IFT of different oil–water system in presence of Tween 20 surfactant

Fig. 5 presents the effect of ZnO NPs on IFT of Tween 20 surfactant at different oil–water systems *viz.*, *n*-hexane–water, *n*-decane–water, *n*-heptane–water, and toluene–water.

It is clear from Fig. 6 that the IFT of different oil–water systems remain almost unchanged in presence of 0.1 weight% of ZnO NPs. This indicates that ZnO NPs are unable to reduce the IFT of different oil–water system. However the IFT of all the oil–water systems decreases in presence of 0.01 mM concentration of nonionic Tween 20 surfactant, as expected. On the contrary the IFT of Tween 20 surfactant increases in presence of ZnO NPs for all the oil–water system studied here. Irrespective of chain length (C$_6$, C$_7$ and C$_{10}$), aliphatic or aromatic (*n*-heptane or toluene), the IFT of Tween 20 surfactant increases in presence of ZnO NPs at different oil–water interface. Similarly behavior is expected for other NPs. Thus, the above results indicate that NPs retard the effectiveness of Tween 20 surfactant in reducing IFT of different oil water systems.

4. Conclusions

In this study, we have compared the effect of different NPs on the IFT of different oil–water system with variation of weight% or/and using a nonionic surfactant: Tween 20. In addition, the
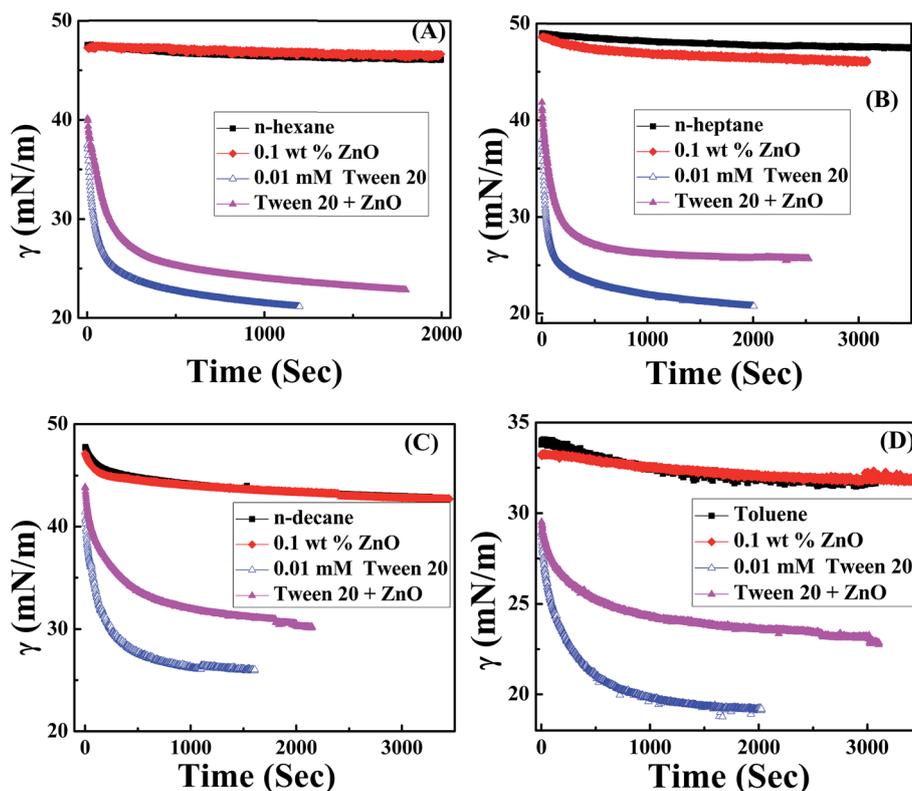
Fig. 6 IFT of Tween 20 surfactants in absence and presence of 0.1 weight% of ZnO NPs at (A) *n*-hexane–water, (B) *n*-heptane–water, (C) *n*-decane–water, and (D) toluene–water interface (standard deviations are less than 1%).

effect of ZnO NPs on IFT of Tween 20 surfactant at different oil–water system was studied. Outcomes of the study are summarized below:

(1) All the three different types of NPs: SiO_2, TiO_2, and ZnO, solely are inactive to reduce the IFT of different oil–water system: *n*-hexane–water, *n*-heptane–water, *n*-decane–water and toluene–water system. The behavior is indifferent to the increase in the weight% of the different NPs.

(2) All the NPs retard the effectiveness of Tween 20 surfactants in reducing the IFT of hexane–water system. The surface excess concentration of surfactants at the interface decreases in the presence of NPs.

(3) For the case of Tween 20 surfactant, increasing the concentration of surfactant increases the D_a, leading to a higher adsorption rate. However D_a, values are less, in presence of NPs compared to the corresponding particle free system, which indicates that the adsorption amount of surfactant at the interface decreases in presence of NPs.

Acknowledgements

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