# Effect of ZnO Nanoparticle and Hexadecyltrimethylammonium Bromide on the Dynamic and Equilibrium Oil−Water Interfacial Tension

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S *Supporting Information*

ABSTRACT: The effect of ZnO nanoparticles on the dynamic and equilibrium interfacial tension in the presence and absence of cationic surfactant CTAB was investigated. The results show that nanoparticles solely have no effect on interfacial tension. However, in the presence of CTAB, both particles and surfactants are adsorbed at the interface, and by a synergistic effect decrease the interfacial tension more. The effect of ZnO nanoparticles on the contact angle and stability of emulsions was studied too. The dynamic interfacial tension data were fitted with two different models. The results show that the adsorption mechanism of surfactant from bulk to interface was controlled by the mixed diffusion-kinetic model.
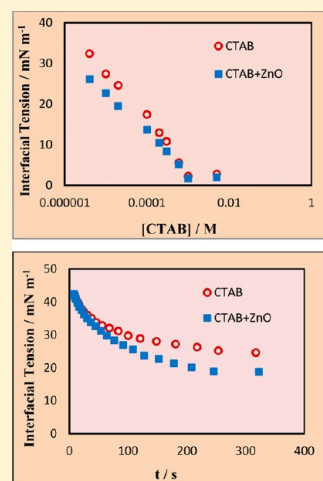
1. INTRODUCTION

Combination of surfactants and nanoparticles and their effect on the air−liquid and liquid−liquid interfaces has been recently considered by researchers due to their importance and also their application especially to improve the stability of emulsions.[1−6] In this regard, various nanoparticles such as silica,[3] bohemite,[7] Fe_3O_4,[8] and TiO_2[9] have been studied. However, despite the importance of nanoparticle adsorption at the air−liquid and liquid−liquid interfaces, so far its mechanism has not been known well. Moreover, the interfacial tension data gives information about the structure and also surface region energy between two phases, so study of interfacial tension is one of the most important cases to understand interactions of particles at the interface.[10] Lan et al.[11] investigated the effect of negatively charged silica nanoparticles on the interfacial tension of CTAB at liquid paraffin−water interfaces. They found that in an appropriate concentration range of CTAB a synergistic effect between nanoparticles and CTAB may reduce the oil−water interfacial tension. Ma et al.[12] studied the effect of these nanoparticles on the surface and interfacial tension with anionic and nonionic surfactants. They showed that nanoparticles can increase the efficiency of the SDS surfactants, whereas they have no effect on the performance of the nonionic surfactants at the oil−water interface. A similar study was carried out by Pichot et al.[10] to know about the effect of hydrophilic silica particles on the interfacial tension in the absence and presence

of tween 60, lecithin, and sodium caseinate at the oil/water interface.

ZnO is one of the compounds which is used in cosmetic products extensively, and therefore, the study of its synergism effect with surfactant molecules and also its effect on the emulsion stability is important.

The purpose of the present work is to study the effect of ZnO nanoparticles on the equilibrium and dynamic interfacial tension in the absence and presence of CTAB. Moreover, in these systems, the static contact angle at three phase boundaries (oil−water−quartz) was studied. Also, the study of dynamic interfacial tension leads to an understanding of the mechanism of CTAB adsorption at the interface in the presence and absence of ZnO nanoparticles. In addition, the effect of ZnO nanoparticles on the emulsion stability with and without CTAB surfactant is one of the other objects that have been considered in the present study.

2. EXPERIMENTAL SECTION

Materials and Methods. The cationic surfactant hexadecyltrimethylammonium bromide, CTAB (≥97%), was purchased from Merck Co. The critical micelle concentration, cmc, in water at 30 °C is 0.9 mM.[3] The oil used in this study was *n*-

decane (from Merck Co., >99%) that was purified by shaking of *n*-decane with water in a separating funnel for 10 min, standing for 20 h, and then separating of *n*-decane up to the interface. Then, it was passed though chromatographic basic alumina to remove polar impurities.[13] The obtained interfacial tension of *n*-decane−water at 25 °C was 48 mN/m, which is in agreement with literature values.[14] ZnO nanoparticles with a diameter of about 20 nm were synthesized according to the literature report[15] and used as the particle component in this study.

ZnO nanoparticles were dispersed (0.01 wt %) in water and aqueous CTAB solution using an ultrasonic (UNIVERSAL ULTRASONIC) for 1 h. The equilibrium and dynamic interfacial tensions between the aqueous phase and oil phase were measured by a DVT30 drop volume tensiometer from Kruss, Germany. The Krafft point of the surfactant is 26 °C,[3] and therefore, the measurements were carried out at 30 °C. The dynamic and equilibrium interfacial tensions for CTAB solution/*n*-decane in the absence and presence of ZnO nanoparticles were measured at different CTAB concentrations. The ZnO nanoparticle concentration was kept constant (0.01 wt %) in all dynamic experiments, but the effect of ZnO on the cmc of CTAB was measured in the three different concentrations of ZnO nanoparticles. Also, all measurements were carried out at pH 7 (pH of CTAB aqueous solution).

The static contact angle of the aqueous phase (including CTAB and ZnO nanoparticles) surrounded by the oil phase was measured at three phase boundaries (oil−water−quartz).

The emulsions of equal volumes of *n*-decane and aqueous solution (including CTAB and ZnO nanoparticles) were prepared with sonication using an ultrasonic probe (SONO-PULS) for 1 min.

3. RESULTS AND DISCUSSION

The SEM image and XRD pattern ZnO nanoparticles are shown in Figure 1. The SEM image shows that particles are spherical with about 20 nm diameter. The XRD pattern shows three characteristic peaks of ZnO at 2θ = 31.6, 34.2, 36.1, 48.1, 56.4, 63.0, 67.9, and 68.9° corresponding to the 100, 002, 101, 102, 110, 103, 112, and 201 planes, respectively.

3.1. Effect of ZnO Particles. The interfacial tension between *n*-decane and water in the presence of ZnO nanoparticles was measured. Figure S1 (Supporting Information) compares the dynamic interfacial tension of water/*n*-decane in the absence and presence of ZnO nanoparticles. It is seen that the presence of ZnO has no effect on the interfacial tension. Figure S2 (Supporting Information) shows the effect of ZnO concentration on the interfacial tension of water/*n*-decane (measured by the ring method). This figure clearly shows that also a high concentration of ZnO has no effect on the interfacial tension, and therefore, ZnO solely (in the absence of CTAB) is not surface active. As it was previously reported, particles can adsorb at the interface but do not change oil−water interactions at the interface, and therefore have no effect on the interfacial tension.[10,16]

3.2. Effect of ZnO Particles in the Presence of CTAB. The dynamic and equilibrium interfacial tension was measured for two systems, which include CTAB aqueous solution/*n*-decane and dispersed ZnO nanoparticles in CTAB solution/*n*-decane, respectively.

3.2.1. Equilibrium Studies. The equilibrium interfacial tension in the absence and presence of nanoparticles (0.01 wt %) has been compared in Figure 2. This figure shows the common interfacial tension curve of surfactants for the pure
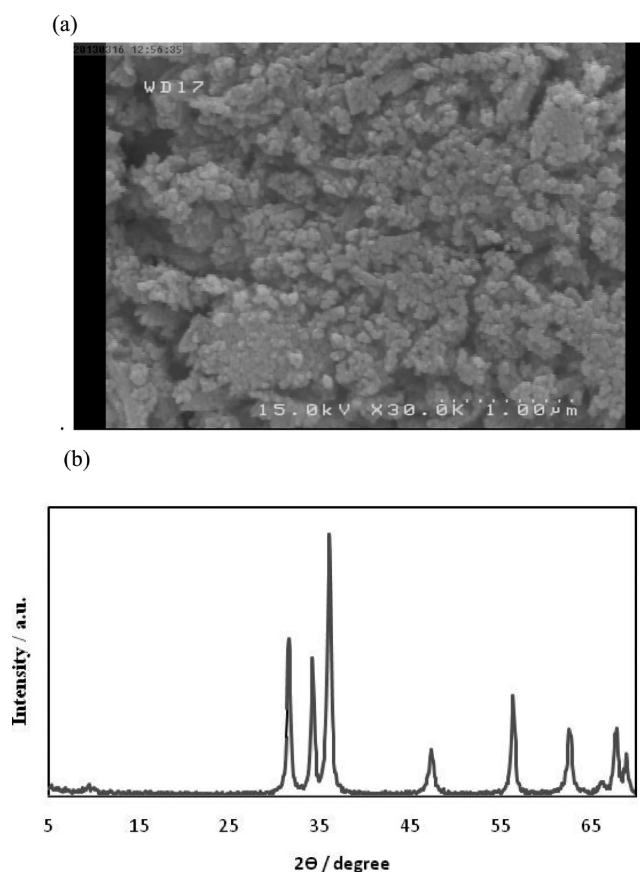
(a)

(b)

Figure 1. (a) The SEM image and (b) the XRD pattern of the prepared ZnO nanoparticles.
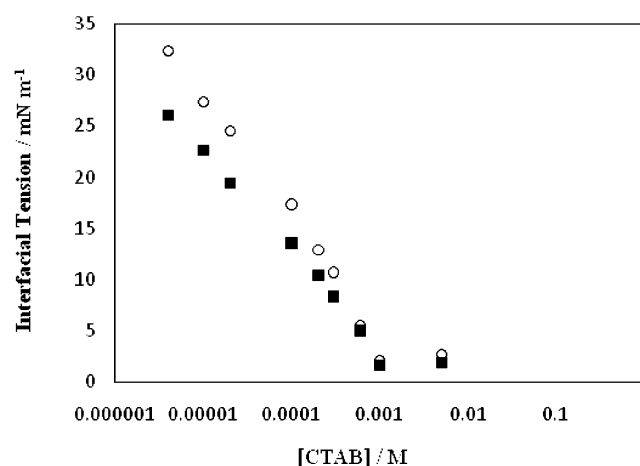

Figure 2. The equilibrium interfacial tension water solution/*n*-decane vs CTAB concentration in the absence (○) and presence (■) of 0.01 wt % ZnO nanoparticles at 30 °C.

CTAB solution with a cmc of about 0.9 mM. However, addition of nanoparticles changes the interfacial tension of the CTAB aqueous solution/*n*-decane. Also, Figure 2 indicates that in the presence of nanoparticles interfacial tension decreases with an increase in CTAB concentration, but the decrease of the interfacial tension is higher than that of the particle free system. It means that the presence of nanoparticles increases the CTAB efficiency to decrease the interfacial tension at all CTAB concentrations. Decreasing the interfacial tension can be

attributed to the synergistic effect of nanoparticles and CTAB to reduce interfacial tension. Adsorption of the surfactant onto nanoparticles increases the hydrophobicity of nanoparticles which further causes these nanoparticles to move toward the interface and remain there.

The effect of ZnO nanoparticles on the cmc of CTAB at three different concentrations of ZnO was studied. The results show that the presence of ZnO nanoparticles has no effect on the cmc (Figure S3, Supporting Information). This result is in agreement with the Lan et al.[11] report, where by increasing of silica nanoparticle concentration the cmc of CTAB was not changed.

The equilibrium surface concentration was calculated from the equilibrium interfacial tension data using the Gibbs equation:

$$\frac{d\gamma_e}{d \ln C} = -2\Gamma_e RT \tag{1}$$

where γ_e is the equilibrium surface or interfacial tension, Γ_e is the equilibrium surface concentration, and C is the bulk concentration. The plot of surface concentration as a function of CTAB concentration in the absence and presence of ZnO particles is shown in Figure 3. For both systems, the Γ_e values
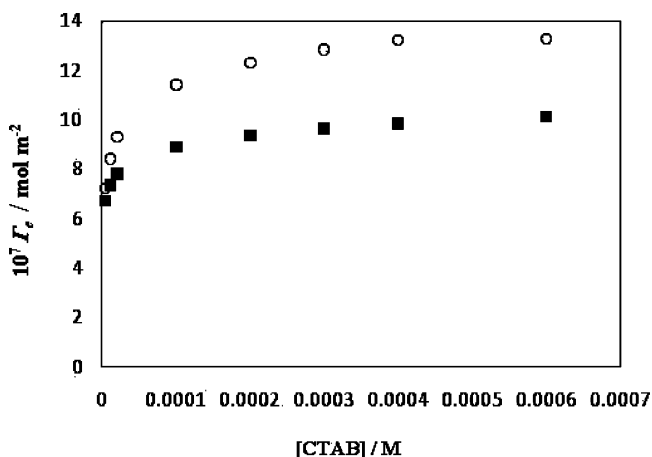
Figure 3. Equilibrium surface concentration vs CTAB concentration in the absence ($\bigcirc$) and presence ($\blacksquare$) of 0.01 wt % ZnO nanoparticles at 30 °C.

increase with CTAB concentration and reach the almost saturated value at the cmc. The equilibrium data were fitted with the Langmuir equation

$$\frac{\Gamma_e}{\Gamma_{sat}} = \frac{KC}{1 + KC} \tag{2}$$

where Γ_{sat} is the saturated surface concentration and K is the Langmuir constant. The results of this fitting are shown in Table 1.

Table 1. The Obtained Parameters of the Langmuir Isotherm for Adsorption of CTAB at 30 °C

system	Γ_{sat} (mol/m^2)	K (L mol^{-1})	r^2
(water + CTAB)/n-decane	1.3×10^{-6}	2.2×10^5	0.9869
(water + ZnO nanoparticle + CTAB)/n-decane	9.7×10^{-7}	4.5×10^5	0.9889

3.2.2. Dynamic Studies. The effect of CTAB in the absence and presence of ZnO nanoparticles on the dynamic interfacial tension between n-decane and water is shown in Figure 4. The
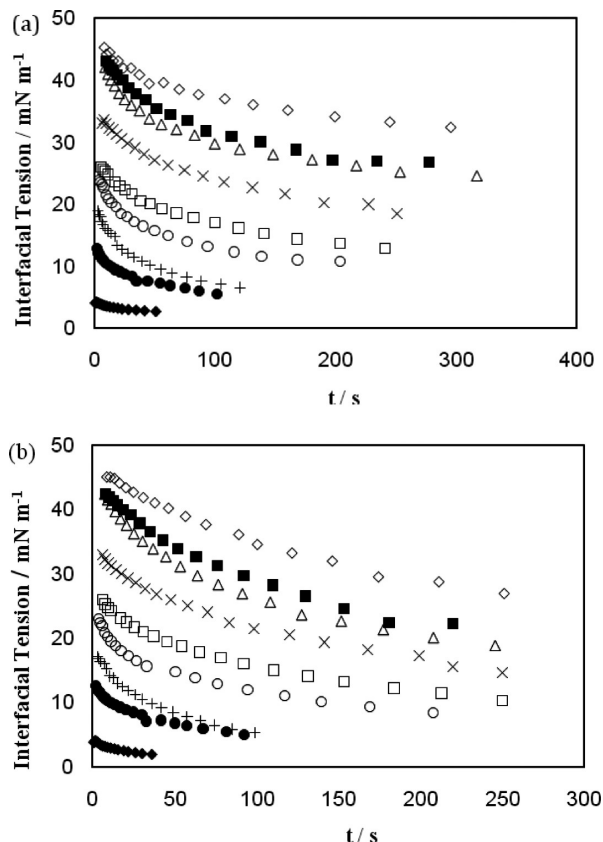
Figure 4. The dynamic interfacial tension of CTAB/n-decane vs time at 30 °C and at different CTAB concentrations, 0.000004 ($\diamondsuit$), 0.00001 ($\blacksquare$), 0.00002 ($\triangle$), 0.0001 ($\times$), 0.0002 ($\square$), 0.0003 ($\bigcirc$), 0.0004 (+), 0.0006 ($\bullet$), and 0.005 ($\blacklozenge$) M: (a) in the absence and (b) in the presence of 0.01 wt % ZnO nanoparticles.

evolution of the interfacial tension with time is very similar for each concentration of CTAB with and without particles. Dynamic interfacial tension is decreased with time; at the initial times, the decrease of interfacial tension is fast, but close to equilibrium, this decrease is slow. Also, for both systems (with and without ZnO), the equilibrium is attained faster at the high CTAB concentration than at low concentration.

The dynamic surface concentration was calculated from the dynamic interfacial tension data and also the following equation (eq 3):[17]

$$\pi = -2k_B T\Gamma_{sat} \ln\left(1 - \frac{\Gamma}{\Gamma_{sat}}\right) \tag{3}$$

In this equation, k_B is the Boltzmann constant, Γ is the dynamic surface concentration, and π is the surface pressure ($\pi = \gamma_0 - \gamma$). Figure 5 shows the change of the surface concentration of CTAB surfactant as a function of time for both CTAB only (Figure 5a) and CTAB with ZnO nanoparticles (Figure 5b) systems. It is seen that, for both systems in the absence and presence of nanoparticles, the surface concentration increases very rapidly at the initial times and then approaches the equilibrium value.
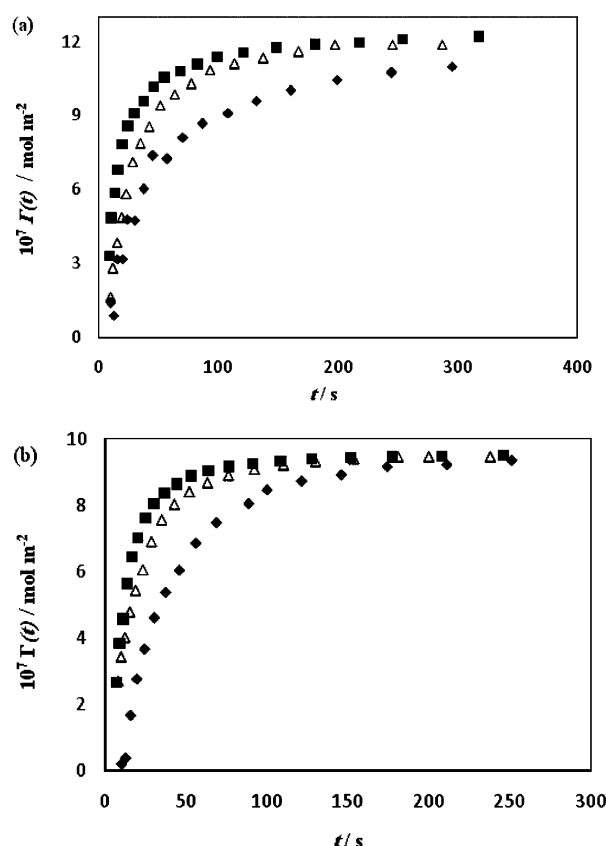
Figure 5. Dynamic surface concentration vs time at different CTAB concentrations, 0.000004 ($\blacklozenge$), 0.00001 ($\triangle$), and 0.00002 ($\blacksquare$) M: (a) in the absence and (b) in the presence of 0.01 wt % ZnO nanoparticles at 30 °C.

By using dynamic surface tension data, it is possible to understand the adsorption mechanism of surfactant from bulk to interface. Therefore, dynamic surface concentrations of CTAB (in the presence and absence of ZnO particles) were fitted with two models when the system is close to equilibrium. The first model that has been derived recently by Azizian[17] based on statistical rate theory (SRT) assumes that the adsorption is the rate controlling step. The relation between surface concentration and time when the system is close to equilibrium based on the SRT model is[17]

$$\frac{\Gamma}{\Gamma_e} + \ln\left(1 - \frac{\Gamma}{\Gamma_e}\right) = \beta - kt \tag{4}$$

where β and k are constants. This equation indicates that the plot of $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$ vs t is a line with k and β as its slope and intercept, respectively. Therefore, the rate constant of surfactant adsorption onto gas/liquid or liquid/liquid interfaces can be easily calculated from the slope of a linear plot. Figure 6 shows the plot of $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$ vs t at specified CTAB concentrations in the absence and presence of ZnO nanoparticles, when the system is close to equilibrium. The same results were observed for other concentrations (data not shown here). Since the mentioned plots are not linear for both systems, it may be concluded that the dynamics of CTAB adsorption (in the absence or presence of ZnO nanoparticles) at the water/*n*-decane interface is not controlled by a pure adsorption mechanism.
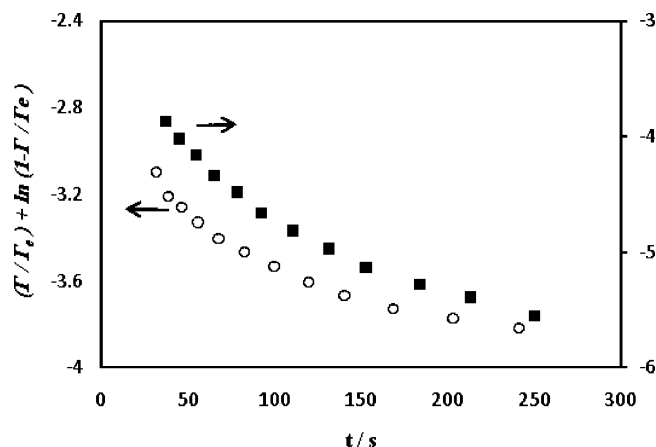

Figure 6. The plot of $(\Gamma/\Gamma_e) + \ln(1 - (\Gamma/\Gamma_e))$ vs time close to equilibrium for 0.0002 M CTAB concentration, in the absence (○) and presence (■) of 0.01 wt % ZnO nanoparticles at 30 °C.

The second model is the mixed diffusion-kinetic-controlled model that was presented by Ward and Tordai[18] and was recently developed by Azizian et al. for close to equilibrium systems.[19] In this model, the relation between dynamic interfacial tension ($\gamma(t)$) and time when the system is close to equilibrium is[19]

$$\gamma(t)_{t\to\infty} - \gamma_e = \frac{RT\Gamma_e^2}{2C_0}\left(\frac{\pi}{f(t)^2 D_a t}\right)^{1/2} \tag{5}$$

where $f(t)$ is defined by[19]

$$f(t) = \frac{\frac{\Gamma_e}{\Gamma_{sat}}\left(1 - \frac{\Gamma_e}{\Gamma_{sat}}\right)}{\frac{\Gamma}{\Gamma_{sat}}\left(1 - \frac{\Gamma}{\Gamma_{sat}}\right)} \tag{6}$$

and D_a is

$$D_a \equiv \frac{D_E^2}{D} = D\exp\left(-\frac{2E_a}{kT}\right) \tag{7}$$

where $\gamma(t)$ is the dynamic interfacial tension, C_0 is the bulk concentration of surfactant, D_a is the apparent diffusion coefficient, D_E and D are the effective diffusion coefficient and the monomer diffusion coefficient, respectively, and E_a is the adsorption activation energy. The values of $f(t)$ were calculated for all concentrations, and in all cases, $f(t) > 0.998$. The plot of $\gamma(t)_{t\to\infty} - \gamma_e$ vs $t^{-1/2}$ at three different concentrations of CTAB has been shown in Figure 7a and b in the absence and presence of ZnO nanoparticles, respectively. The linearity of these figures indicates that the adsorption mechanism of surfactant from the bulk to the interface was controlled by a mixed diffusion-kinetic model. This means that the migration rate of surfactant to the interface is controlled by both diffusion and adsorption mechanisms. The apparent diffusion coefficient, D_a, can be derived directly from the slope of plots for close to equilibrium systems based on eq 5. Figure 8 compares the apparent diffusion coefficient, D_a, as a function of surface concentration for systems containing CTAB only and CTAB with ZnO nanoparticles. As it can be seen, in both cases, the behavior of D_a is similar. The diffusion coefficient decreases by increasing the CTAB concentration at the interface, and then, it reaches a constant value at the higher concentrations. However, by comparing two plots, we can see that, in all
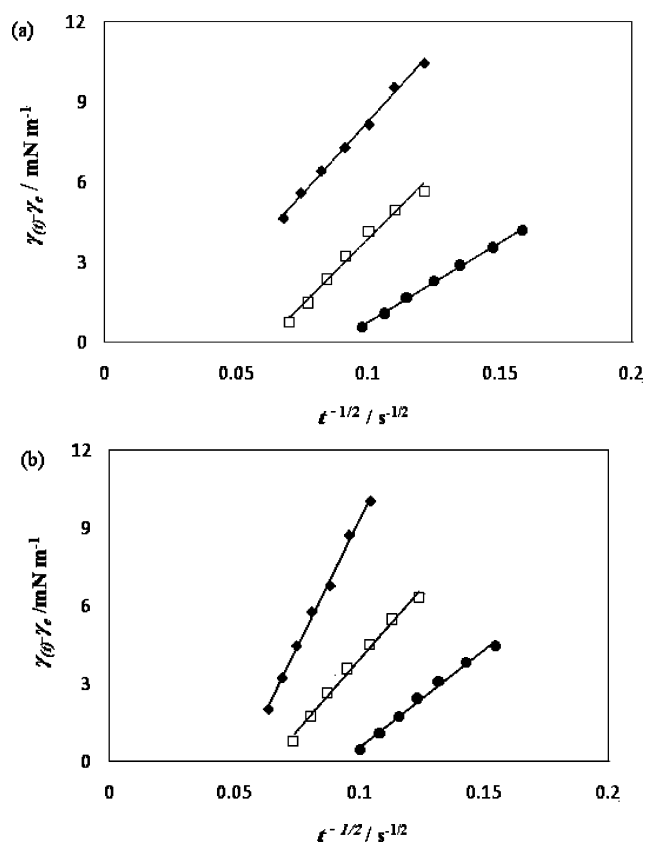
(a)

(b)

Figure 7. Plot of $\gamma(t)_{t\to\infty} - \gamma_e$ vs $t^{1/2}$ for close to equilibrium data at three different concentrations of CTAB, 0.00002 (◆), 0.0002 (□), and 0.0004 (●) M: (a) in the absence and (b) in the presence of 0.01 wt % ZnO nanoparticles at 30 °C.
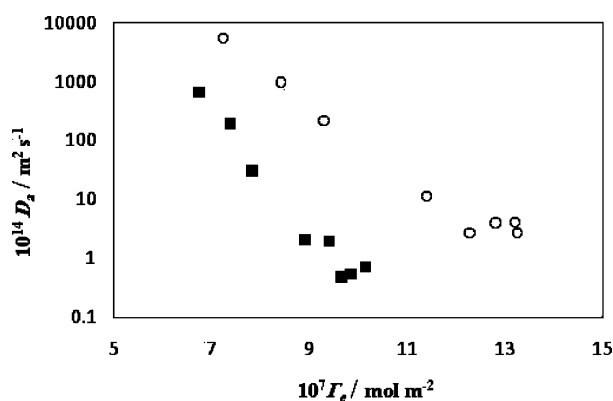

Figure 8. Apparent diffusion coefficient D_a vs Γ_e for CTAB in the absence (○) and presence (■) of ZnO nanoparticles at 30 °C.

concentrations of CTAB, D_a in the presence of nanoparticles is less than that when there is no particle in the solution. The value of effective diffusion coefficient, D_E, can be calculated by using eq 6. Accordingly, the behavior of D_E is similar to that of D_a for both systems (Figure 9). Also, the activation energy, E_a, can be calculated similarly from eq 6. The changes of E_a with the surface concentration (Γ_e) at 30 °C have been plotted in Figure 10 for systems containing CTAB only and CTAB with ZnO particles. This figure shows that E_a is zero at low surface concentrations and increases with increasing surface concentration. This means that at the low surface concentrations diffusion is the only rate-controlling step in the adsorption
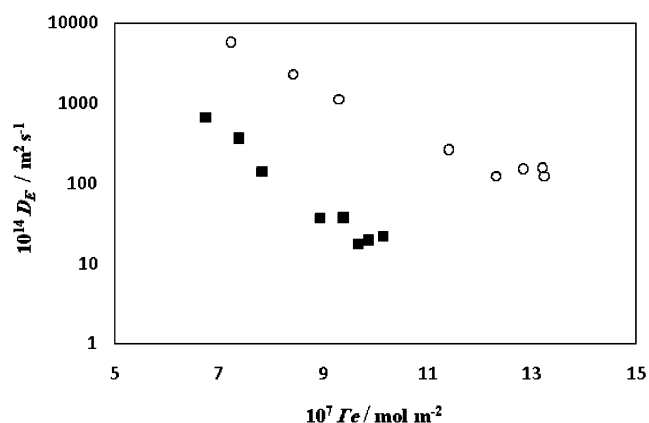

Figure 9. Effective diffusion coefficient D_E vs Γ_e for CTAB in the absence (○) and presence (■) of ZnO nanoparticles at 30 °C.
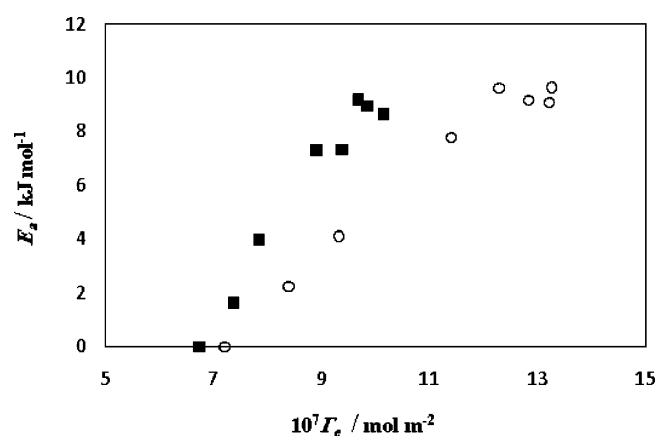

Figure 10. Activation energy of adsorption, E_a, vs Γ_e in the absence (○) and presence (■) of ZnO nanoparticles at 30 °C.

kinetics, because the surface is empty and no activation energy is required for adsorption of surfactant molecules from the subsurface to the interface. On the other hand, by increasing Γ_e, the rate of adsorption from the subsurface to the interface decreases and becomes comparable with diffusion from the bulk to the subsurface and thus the adsorption mechanism becomes a mixed diffusion-kinetic control. It is also noted in Figure 10 that the activation energy of adsorption is decreased in the presence of ZnO nanoparticles. This means the presence of a synergism effect between CTAB and ZnO nanoparticles which caused a decrease of the activation energy for adsorption.

3.3. Effect of pH. The pH of the point of zero charge (pH_{pzc}) for ZnO nanoparticles was determined by the Faria et al. method.[20] The obtained value of the point of zero charge for ZnO nanoparticles is 7. This means that at pH > 7 the surface charge is negative and at pH < 7 the surface charge of ZnO nanoparticles is positive. Figure 11 shows the interfacial tension of (CTAB solution + ZnO nanoparticle)/n-decane as a function of time at three different pH's. As can be seen at pH 10 and 5, the decrease of the interfacial tension is higher than that at pH 7. At pH 10, CTAB with a cationic headgroup adsorbed onto nanoparticles with a negative surface charge and by migration to the interface cause a higher decrease of the interfacial tension.[11] At pH 5, the repulsive Coulomb forces between the positively charged nanoparticles and positively charged CTAB promote the surfactant diffusion toward the interface and decrease the interfacial tension.[12]
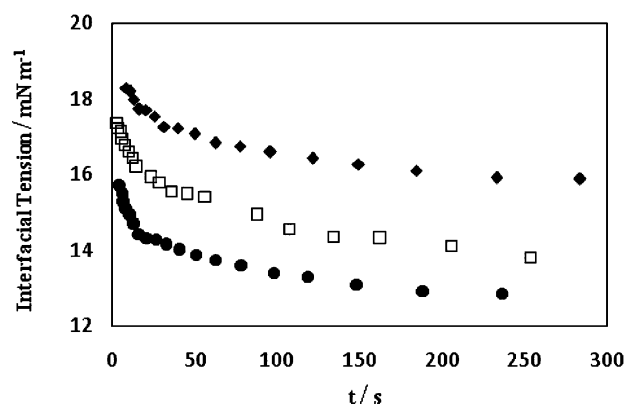
Figure 11. Effect of solution pH on the dynamic interfacial tension (0.00004 M CTAB + ZnO nanoparticles)/n-decane: pH 5 ($\square$), pH 7 ($\blacklozenge$), and pH 10 ($\bullet$) at 30 °C.

3.4. Three-Phase Contact Angle. The effect of CTAB concentration on the contact angle in the absence and presence of ZnO nanoparticles was investigated too. As can be seen in Figure 12 for both systems containing CTAB and CTAB with
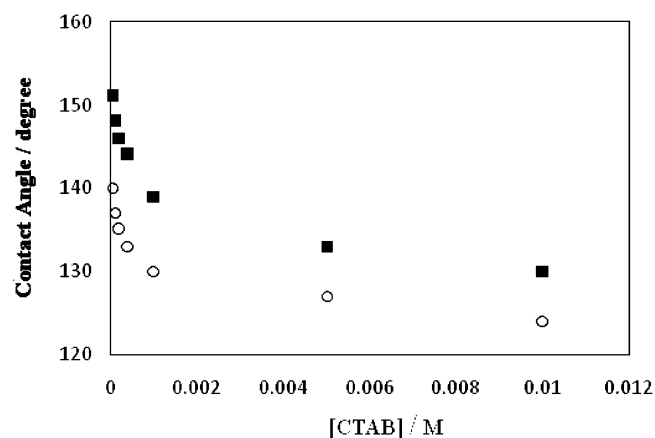

Figure 12. Effect of CTAB concentration on the static contact angle in the absence ($\bigcirc$) and presence ($\blacksquare$) of ZnO nanoparticles.

nanoparticles, the contact angle decreased with increasing CTAB concentration; this decrease is higher at the lower concentrations of CTAB. Comparing the two plots shows that the contact angle for systems with nanoparticles is higher than the particle-free system. Also, the difference between the two systems decreases with increasing CTAB concentration. The higher value of contact angle in the presence of nanoparticles can be attributed to the decrease of interfacial tension (γ_{OW}), according to the Young equation:

$$\cos\theta = \left(\frac{\gamma_{OS} - \gamma_{WS}}{\gamma_{OW}}\right) \tag{8}$$

where γ_{OS} and γ_{WS} are the interfacial tension of oil/solid and water/solid, respectively. For systems with nanoparticles, the oil/water interfacial tension is lower than the particle-free system ($(\gamma_{OW})_{CTAB+ZnO} < (\gamma_{OW})_{CTAB}$) that was described in the previous sections; therefore, according to eq 8, the contact angle is higher in the presence of ZnO nanoparticles.

3.5. Emulsions Stability. In this section, the effect of nanoparticles on the emulsion stability with and without CTAB is studied. For this purpose, equal volumes of water (including

ZnO or CTAB or a mixture of ZnO and CTAB) and n-decane were mixed with an ultrasonic probe. Figure 13a shows the
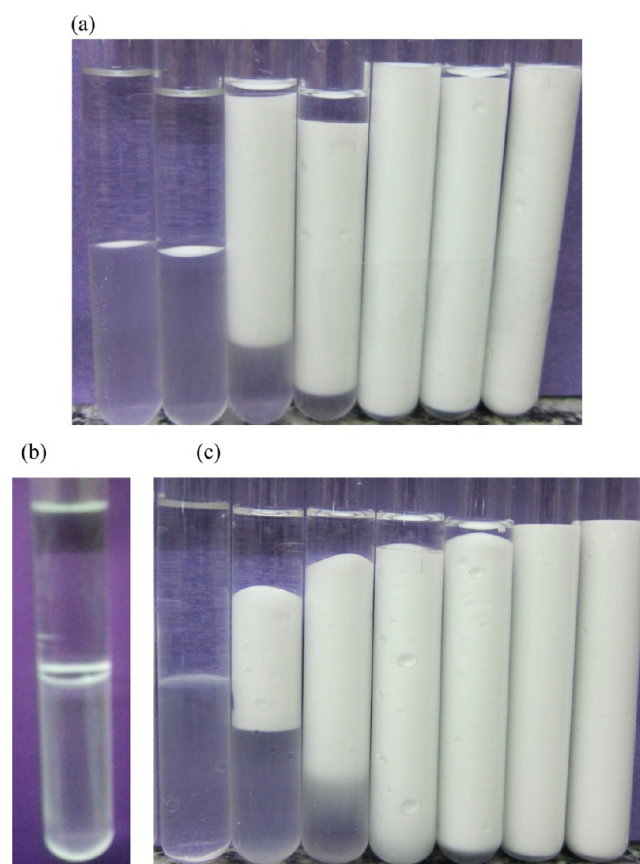

Figure 13. Photograph of vessels containing emulsions of decane and water (1:1) stabilized by (a) CTAB surfactant alone at concentrations of 0.00001, 0.00005, 0.0002, 0.0004, 0.001, 0.05, and 0.01 M (left to right). (b) ZnO nanoparticles (0.01 wt %) alone. (c) A fixed concentration of ZnO nanoparticles (0.01 wt %) and CTAB with the same concentrations as part a.

image of emulsions containing CTAB, 24 h after preparation. It is clear that the CTAB is a good emulsifier particularly at high concentrations. Figure 13b shows the image of emulsion in the presence of ZnO nanoparticles alone, it can be seen that ZnO nanoparticles solely are poor emulsifiers due to their hydrophilic character and disability for remaining at the interface. On the other hand, the image of emulsions in the presence of 0.01% ZnO particles after 24 h at various concentrations of CTAB has been shown in Figure 13c. This figure indicates that ZnO nanoparticles at the low CTAB concentration slightly enhance the stability of emulsion. This observation may be related to the increase of the hydrophobic character of the particles by the adsorption of CTAB molecules onto the nanoparticle surface. Optical microscopy images of emulsions including ZnO nanoparticles (a), CTAB (b), and their mixture (c–e) are given in Figure 14. It can be observed that all drops are spherical and discrete, and in image a (ZnO emulsifier), the drop size is smaller than that in image b (CTAB emulsifier). Also, in the presence of ZnO nanoparticles, the drop size decreased by increasing CTAB concentration. These observations are similar to the results of Binks et al. for silica nanoparticles.[3]
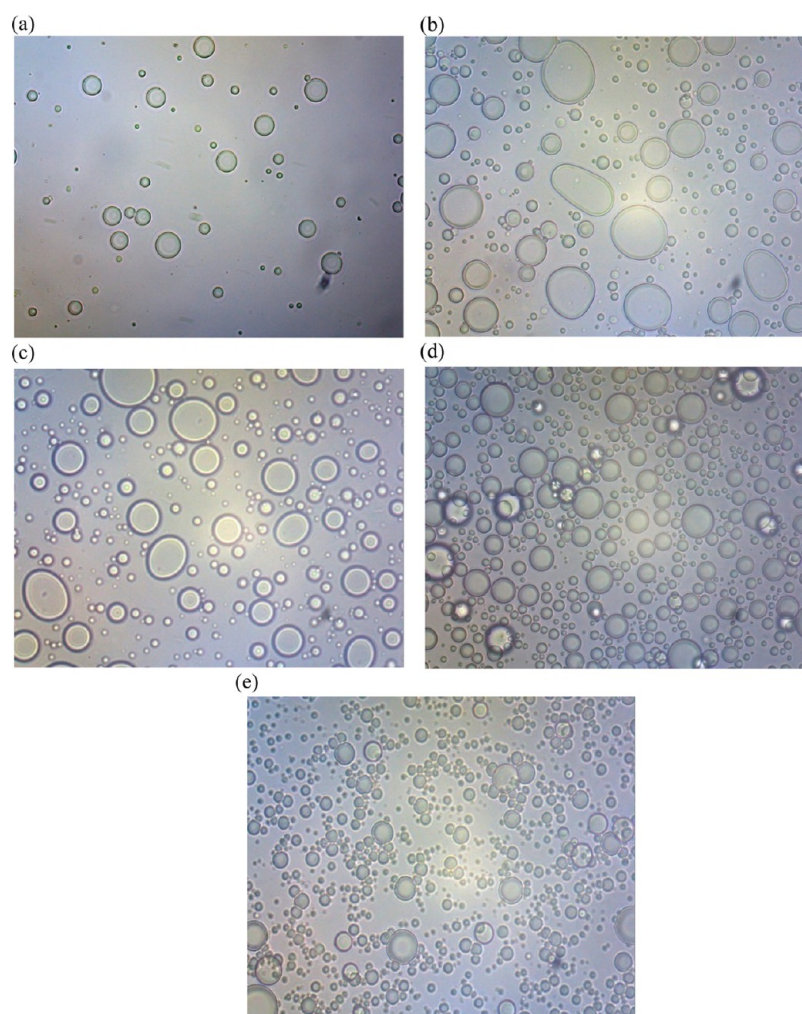
Figure 14. Optical microscopy image of *n*-decane-in-water emulsions (1:1) stabilized by (a) 0.0004 M CTAB alone, (b) 0.01 wt % ZnO particles alone, and a mixture of 0.01 wt % ZnO particles and (c) 0.00005, (d) 0.0002, and (e) 0.0004 M CTAB. With ×400 magnification.

4. CONCLUSIONS

The effect of ZnO nanoparticles on the dynamic and equilibrium interfacial tension in the presence and absence of cationic surfactant CTAB was investigated. The results showed that ZnO nanoparticles solely have no effect on interfacial tension. However, in the presence of CTAB, particles affect the interfacial tension. Nanoparticles increase the CTAB efficiency in decreasing the interfacial tension due to the synergistic effect. Adsorption of CTAB onto nanoparticles changes the surface of ZnO from a hydrophilic to hydrophobic surface. The presence of nanoparticles also affects the dynamic interfacial tension; nanoparticles increase the rate of decreasing interfacial tension. The dynamic interfacial tension data were fitted with two models; the results of fitting indicate that the adsorption mechanism of surfactant from the bulk to the interface is controlled by a mixed diffusion-kinetic-controlled model. Also, the results show that ZnO nanoparticles are poor emulsifiers, but at a low concentration of CTAB, the emulsion stability is enhanced slightly.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The plots for the effect of ZnO nanoparticles on the water/*n*-decane interfacial tension and the effect of ZnO nanoparticle concentration on the cmc of CTAB. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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