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Study on Stabilizing Emulsion by Mixing Nano-silica and Cationic Surfactants with Different Chain Length

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Abstract. Considering the interaction between the electronegative nano-silica (NS) and cationic surfactant, this paper aims at studying the effect of NS modified by cationic surfactants with different chain length on emulsion behavior. These effects on emulsion behavior were investigated at two aspects: emulsion stability and rheological characteristics. Experimental results indicated that flocculation of nano-silica becomes easier with longer alkane chains. While the chain length increases within the studied concentration range, the threshold concentration of surfactants at which the intermediate phase emulsion appears decreases. For NS and DETAB together in dispersion, no phase inversion appeared. The NS surface hydrophilic-lipophilic balance was changed due to the enwind of the alkane chain. Longer alkane chain adsorbs on the NS surface and reaches saturation at the same surfactant concentrations more easily due to the different enwind degrees of alkane chains. It is suggested that the different surfactant chains had different enwind degrees on the liquid-liquid interface. Rheological experiments show that the emulsion has shear dilution and elasticity.

1. Introduction

Emulsions have been widely applied in many fields including enhanced oil recovery processes, cosmetics, chemistry engineering and food industries [1-2]. The instability of emulsions is a critical issue in all these applications. Emulsion instability arises from the coalescence of oil or water droplets [3]. Thus, it is crucial to solve the problem of emulsion instability. Pickering emulsions were first put forward in 1907 [4]. Pickering emulsions are much similar with surfactant-based emulsions but more stability. Solid particles absorb at the liquid-liquid interface to stabilize emulsion by preventing droplets coalescence [5].

Some colloid particles, like hydrophilic nano-silica, are hard to assemble to oil-water interface. There are three ways to change nanoparticles (NPs) activity including (1) modification of surface roughness of NPs [6], (2) chemical grafting by synthesis reaction [7], and (3) physical modification by electrostatic interaction [8]. Physical modification has been studied in many reports. Recent studies have focused on the synergy between various nanoparticles and surfactants to stabilize emulsion. Silica particles, alumina particles and CaCO₃ nanoparticles [9-12] combined with cationic or anionic surfactants have been studied. Surfactants were used as surface modifiers to change the surface activity of NPs [13] when adsorbing at their surfaces. Surfactants type and concentration determine the surface activeness of NPs [10]. The self-assembled nanoparticles can exist strongly at both liquid-liquid and gas-liquid [14] surfaces.

The nano-Al as stabilizer to stabilize nano-emulsion was investigated by Mehta et al [10]. The most efficient surfactant as surface modifier forming the nano-emulsion was determined by measuring their



interfacial tensions. Zeta potential values proved that particles had adsorbed on water-diesel interface. Dai et al [9]. studied the synergy mechanism between silica nanoparticles with dimethyldodecylamine oxide (OA-12) to enhance the emulsion stabilization and revealed that the adsorption surfactant changed the hydrophilic-lipophilic balance of NPs surfaces. Phase inversion was observed due to the bi-layer surfactant adsorption on NPs surface. Cui Z G et al [11]. studied double phase inversion of emulsions stabilized by hydrophilic CaCO_3 nanoparticles and anionic surfactant-sodium dodecyl sulphate (SDS). With the concentration of SDS increased, double phase inversion occurred from O/W to W/O to O/W again due to further adsorption of SDS. Binks B P et al [12]. investigated the behavior of emulsions stabilized by a mixture of silica nanoparticles and cationic surfactant (CTAB). At different pH, the emulsions stabilized by particles, surfactant and the synergy of particles and surfactant. The contact angle measurements at interfaces proved that silica surfaces become increasingly hydrophobic initially with addition of surfactant. The presence of surfactant altered the activity of NPs surface.

The mixtures between different cationic surfactants with silica particles have been studied and focused on their behaviors and surface properties. But the effects of different chain length surfactant on NPs interface activity were less researched. The purpose of this work is to understand how the alkane chain length influenced the behavior of dispersions and emulsions. DETAB, TTAB and CTAB were chosen as the representatives of different chain length surfactants. Considering the synergy between nano-silica(NS) and surfactants, which can generate NS-surfactant, the influence of different chain length on emulsion behavior was analyzed systematically.

2. Materials and methods

2.1. Materials

Cationic surfactants with different chain length, Decyltrimethylammonium bromide (DETAB), Myristyl trimethyl ammonium Bromide (TTAB) and Hexadecyl trimethyl ammonium Bromide (CTAB), were used in experiments. The bare silica NPs(SNP) (LUDOX HS-30, Sigma-Aldrich) was purchased as 30 wt% solution. N-dodecane (Aladdin Biochemical Technology Co., Ltd (Shanghai, China)) was chosen as oil phase.

2.2. Methods

To ensure the accuracy of solution concentrations, high concentrations of the three surfactants (0.01mol/L) were first prepared and stirred. The concentration range of three surfactants solutions was from 0.05 mmol/L to 9 mmol/L. First of all, portions of the three surfactants were weighed from high concentration surfactant solution into glass bottles and diluted with ultrapure water. Then a certain amount of silica NPs were calculated and added into the surfactant solutions drop by drop. Finally, the solutions were stirred to fully disperse. The ULTRA-TURRAX homogenizer was used to prepare the emulsions with a stirring speed at 10000 rpm for five minutes. The oil and water at a volume ratio of 1:1 were prepared in glass bottles. After homogenization and stabilization, the volume of emulsions was observed and recorded to determine the emulsification ability of NPs modified by surfactants. The volume of emulsions was recorded every ten minutes to observe the stability of the emulsions. Rheological measurements were performed using a coaxial cylinder sensor system equipped Haake RS6000 rheometer. The steady shear and oscillatory measurements were carried out to explain the stability of emulsions.

3. Results and Discussion

3.1. Dispersion of solution

The 0.5 wt % NS with different surfactant concentrations were prepared as aqueous solutions to form the emulsion. With the surfactants concentration increase, the agglomeration degree of dispersions was substantially changed. The surface property of the NS was changed due to the adsorption of cationic

surfactant. The solutions were prepared by cationic surfactant and NS are given in Figure 1. As shown in Figure 1, it can be seen that solutions were transparent at low surfactants concentrations. Under this circumstance, the surface of NS is mainly hydrophilic. Only a small amount of cationic surfactants adsorbed on the surface of NS, which is not enough to reverse the hydrophilic of particles. The electrostatic repulsion between particles dominates, and thus the flocculation of NS did not appear. As the concentration of surfactants increases, dispersions become turbid and produce a certain amount of flocculation. In this time, NS are completely hydrophobic. The adsorption of surfactants on the surface of NS gradually saturated. The strong van der Waals attraction between the alkane chains of surfactants on adjacent particle caused the flocculation. The volume of flocculation reached the maximum. When the concentration of surfactants continues to increase, the volume of flocculation decreases. Electrostatic interaction dominated the adsorption process and made the particles hydrophilic again [15]. Within the studied concentration range, the volume of flocculation tended to stable at a relatively low level in the end. For solutions of NS-DETAB, NS-TTAB and NS-CTAB, the flocculation appeared when the concentration exceeded 3, 0.5 and 0.1 mmol/L, respectively. The longer the alkane chain, the lower concentration of surfactants when solution begin to flocculation. It can be inferred that the hydrophobicity of NS enhanced with the chain length of surfactants increases. Because longer alkane chains are easier to entangled with other alkane chains on the surface of NS and hence will occupy more surface area of NS. Therefore, longer alkane chain will adsorb and saturate on the surface of NS at the low surfactants concentration. As the shortest chain surfactant, DETAB solution was still transparent and bluish when the maximum flocculation volume appeared of TTAB and CTAB. DETAB show good dispersion.

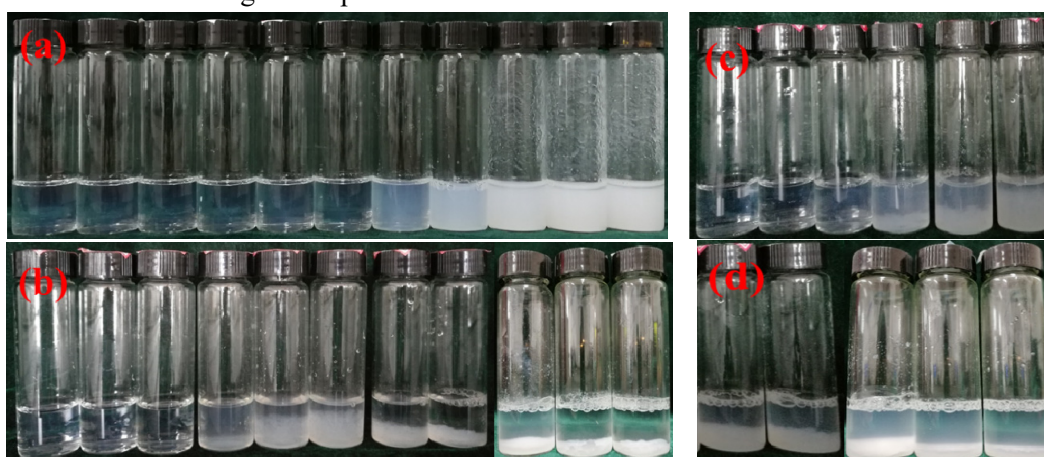


Figure 1. The solutions of (a) DETAB, (b) TTAB and (c) (d) CTAB with a concentration are as follow: 0.01, 0.05, 0.1, 0.5, 1, 1.5, 3, 4.5, 6, 7.5 and 9 mmol/L. The concentration decreases from left to right (0.5 wt % NS).

3.2. Phase inversion of emulsions

The emulsions mixed of different NS-surfactants (0.5 wt % NS) with n-dodecane were displayed in Figure 2. It can be seen that the volume of emulsions increased first and then decreased. Phase inversion did not occur for emulsions stabilized by DETAB and NS and emulsions are all o/w type. Emulsion of TTAB and CTAB were significantly changed to the intermediate phase emulsion at the concentration of 5.5 and 4.2 mmol/L respectively. The concentration of surfactants determines the hydrophilic-lipophilic characteristic of NS surface. The length of alkane chain also had influence on NPs surface characteristic due to different enwind degree. The alkane chain of DETAB was not long enough and the enwind degree was not high enough to change the hydrophilic-lipophilic characteristic of NS surface. The emulsion behavior of TTAB and CTAB was different from DETAB. When the concentration of TTAB is less than 5.5 mmol/L, the type of emulsions is o/w. The surface of NS adsorbed so little surfactant that the hydrophilicity of NPs cannot be totally changed. At

concentrations of TTAB between 5.5 and 6.5 mmol/L, emulsions existed as an intermediate phase and the surface of NS achieved adsorption saturation. NS tends to stable w/o emulsions due to the NS are hydrophobic. At this time, o/w emulsion began to change to w/o emulsion and then the intermediate phase emulsion was observed. Above 6.5 mmol/L, emulsions became o/w type again because the NS formed with a double layer adsorption on the surface and became hydrophilic. For CTAB, surfactants concentrations of the intermediate phase emulsion ranged from 4.2 to 4.7 mmol/L. The concentration of intermediate phase emulsion is lower than the TTAB. It can be attributed to the length of alkane chain. The other studied concentrations of CTAB emulsions were all o/w type. These phenomenons of CTAB were the same with TTAB and proved the theory of the degree of adsorption on the surface of NS. Emulsions of NS mixtures with different chain length surfactants had different phase inversion concentration. With the alkane chain length increases, the phase inversion concentration decrease. Longer alkane chain on the surface of particles tend to cover more surface area. The degree of adsorption also depended on the chain length of surfactant. At the same concentration, longer alkane chain can easily absorb and reach saturation. Thus, longer chain can easily change the hydrophilic-lipophilic of the NS. These is well coordinated with the theory of enwind degree of the alkane chain.

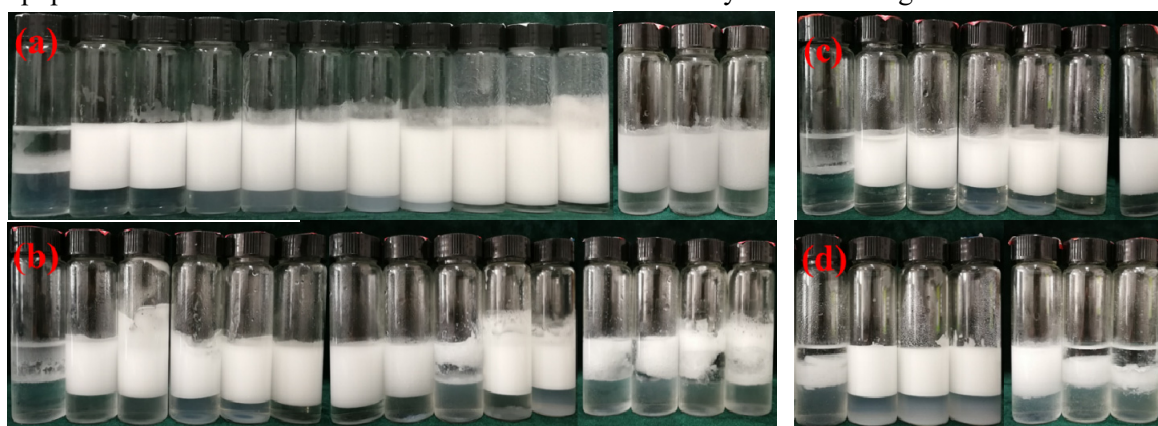


Figure 2. emulsions stabilized by NS and surfactants. Concentration are as follow: (a) DETAB 0.01, 0.05, 0.1, 0.5, 1, 1.5, 3, 4.5, 6, 7.5, 9, 10, 12 and 15 mmol/L, (b) TTAB 0.01, 0.05, 0.1, 0.5, 1, 1.5, 3, 4.5, 6, 7.5, 9, 5.5, 5.7, 6.5 and 6.7 mmol/L, (c) CTAB 0.01, 0.05, 0.1, 0.5, 1, 1.5, 3 mmol/L, (d) CTAB 4.5, 6, 7.5, 9, 4, 4.2 and 4.7 mmol/L.

3.3. Steady shear and oscillatory measurements

The emulsions with surfactants concentrations of 0.05, 1.5, 4.5 and 7.5 mmol/L and silica NPs of 0.5 wt% were used to conduct rheological measurements. The viscosities of emulsions stabilized by different chain length surfactants with different shear rates are shown in Figure 3. The shear thinning behavior was observed and appeared with the increase of shear rate. This phenomenon can attribute to the cracking of emulsions. The shear viscosities of emulsions were distinct for different chain length surfactants. The chain length of surfactants has influence on the shear viscosities. The shear viscosities of emulsions stabilization by DETAB and 0.5 wt% NS is shown in Figure 3(a). The shear viscosities decreased with the increase of surfactants concentration because emulsions were all o/w type in the four studied concentrations. Therefore, it can be concluded that for the same type emulsion, as the concentration of surfactant increased, the shear viscosities of emulsions increased as well. Unlike DETAB, TTAB and CTAB shown different phenomenon in Figure 3(b) and Figure 3(c). With the increase of surfactant concentration, the shear viscosities increased first and then decreased. When emulsion appears as an intermediate phase, the maximum shear viscosity appeared at a surfactant concentration of approximately 4.5 mmol/L. The intermediate phase emulsion contains both o/w and w/o emulsions. The o/w or w/o emulsion was broken and ultimately stable in one type of emulsion under shearing. The o/w emulsions were destroyed under shearing, and thus the viscosities of the emulsions decreased. The type of emulsions determines their shear viscosities. During modulus

measurement, the stress and strain change with time were measured by applying sinusoidal shear to the emulsion with small amplitude oscillation. Storage modulus (G') and loss modulus (G'') were obtained. For the two modulus, the former is related to the elasticity of emulsion and the latter is linked to the viscosity of emulsion. Comparing the magnitudes of two modulus, which of the viscosity and elasticity of emulsion played a main role under certain conditions can be determined. As seen in Figure 4, the storage modulus is all greater than the loss modulus in three different chain length surfactants stabilized emulsions. It can be inferred that the elasticity of emulsions plays a main role. At this time, emulsions exhibited a similar elastic rheological behavior like gel. The change patterns of the storage modulus and loss modulus were not the same when the chain length of the surfactant is different. For four different concentrations of DETAB, as shown in Figure 4(a), both storage modulus and loss modulus enhanced along with the increase of concentration. However, unlike DETAB, the storage modulus and loss modulus of emulsions contained CTAB and TTAB increased first and then decreased with the growth of concentration. The surfactants concentration at around 4.5mmol/L when the maximum modulus appeared. As for shear viscosities, emulsions contained CTAB and TTAB also showed the same phenomenon. Thus, it can be concluded that the storage modulus seems to be related with the stability of emulsions: the higher the storage modulus is, the more stable emulsions are.

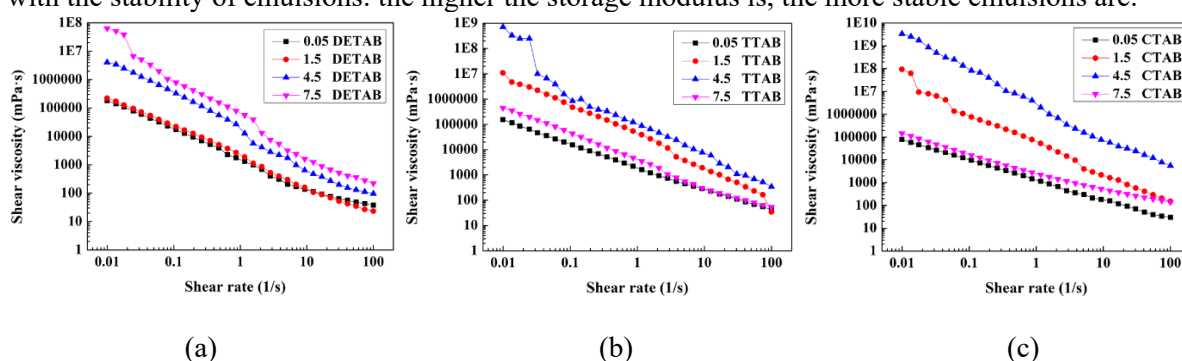


Figure 3. Shear viscosities of emulsions stabilized by NS and (a) DETAB (b) TTAB (c) CTAB at concentrations as follow: 0.05, 1.5, 4.5 and 7.5mmol/L.

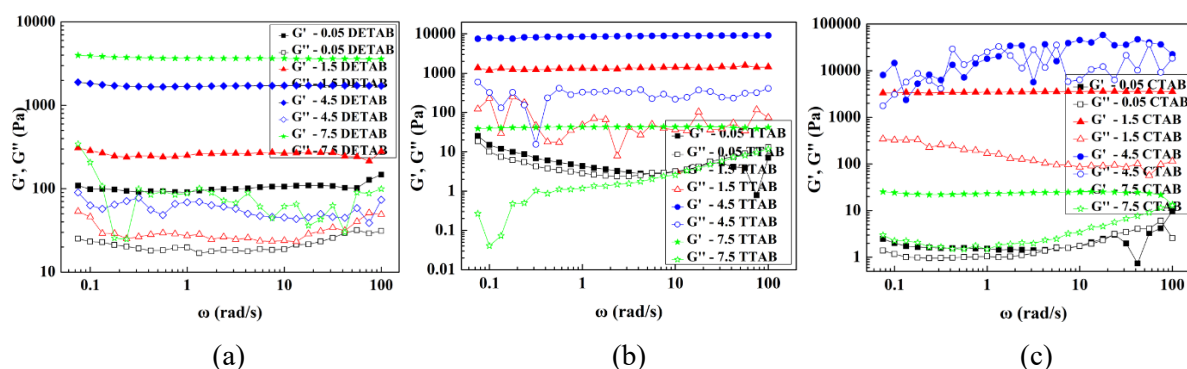


Figure 4. The relationship between the angular velocity with the storage modulus (G') and loss modulus (G'') of emulsions modified by (a) DETAB (b) TTAB (c) CTAB and 0.5 wt % NS.

4. Conclusion

This work was to study different chain length cationic surfactants stabilizing emulsions by adding electronegative NS. The emulsion stability, phase inversion and rheological characteristics were investigated. In the experiments, all the emulsions showed fine stability due to the interaction between NS and surfactant. The intermediate phase emulsion of different surfactants appeared due to the change of the hydrophilic-lipophilic characteristic of NS surface. The enwind degree of the surfactant alkane chain determined the hydrophilic-lipophilic characteristic. The concentration of the intermediate phase emulsion decreased with the surfactant alkane chain increase. Emulsion stabilized by NS and cationic surfactants showed shear dilution and good elasticity.

Acknowledgments

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