

Modification and investigation of silica particles as a foam stabilizer

Qian Zhu, Hua-lei Zhou, Ying-xiao Song, Zhi-dong Chang, and Wen-jun Li

School of Chemistry and Biological Engineering, University of Science and Technology Beijing, Beijing 100083, China
(Received: 22 July 2016; revised: 14 September 2016; accepted: 17 October 2016)

Abstract: As a solid foam stabilizer, spherical silica particles with diameters ranging from 150 to 190 nm were prepared via an improved Stöber method and were subsequently modified using three different silane coupling agents to attain the optimum surface hydrophobicity of the particles. Fourier transform infrared (FTIR) spectra and the measured contact angles were used to characterize the surface properties of the prepared particles. The foam stability was investigated by the foam drainage half-life and the expansion viscoelastic modulus of the liquid film. The results demonstrate that all of the modified silica nanoparticles effectively improve the foam stability. The surface hydrophobicity of the modified particles is found to be a key factor influencing the foam stability. The optimum contact angle of the particles lies in the approximate range from 50° to 55°. The modifier molecular structure used can also influence the stabilizing foam property of the solid particles. The foam system stabilized by (CH₃)₂SiCl₂-modified silica particles exhibits the highest stability; its drainage half-life at maximum increases by 27% compared to that of the blank foam system and is substantially greater than those of the foam systems stabilized by KH570- and KH550-modified particles.

Keywords: silica; nanoparticles; surface modification; hydrophobicity; foam stability; viscoelasticity

1. Introduction

Foam is defined as a gas system isolated by continuous liquid films and is widely used in the cosmetics industry, mineral flotation, fire suppression, etc. [1–3]. In the previous decades, some scientists and engineers probed and investigated its potential use in tertiary oil recovery [4–6]. In general, foam systems are thermodynamically unstable, and their long-term stability is commonly a prerequisite for their successful application.

Gravitational liquid drainage and bubble coalescence due to gas diffusion through the liquid film are pivotal factors leading to bubble burst [7]. To improve the foam stability, additives such as surfactants, macromolecule polymers, or even solid particles have been introduced into the foaming solution [8–9]. Compared with surfactants and macromolecules, solid particles have exhibited the unique advantage in improving the foam stability. In principle, a solid film or a film with a bridging network structure that forms at the gas–liquid interface can substantially increase the film thickness and strength by effectively thwarting gas diffusion and liquid discharge [10–12]. However, the application of a

solid foam stabilizer in nanometric particle size and its potential use in tertiary oil recovery remain immature, waiting for in-depth cultivation in further.

Hydrophobicity is a critical property of solid particles used as a foam stabilizer. Dong *et al.* [13] modified spherical silica particles with cetyltrimethylammonium bromide (CTAB) and used them to stabilize foam. They proposed that the foam stability increased with increasing quantity of CTAB adsorbed onto the silica particles. Bink and Horozov [14] found that the most stable foam was attained when 68% of –OH groups on the silica nanoparticle surface were covered by hydrophobic groups. Typically, the contact angle is used to quantitatively study the surface hydrophobicity of solid particles [15]. Kaptay [16] reported that the optimal contact angles ranged from 50° to 90° and the hydrophobicity strongly affected the foam stabilizing capability of solid particles.

Inorganic particles such as silica particles have been widely used as a foam stabilizer because of their favorable attributes, including large surface energy, easy modification, good chemical stability, and low cost [17]. To obtain silica particles with appropriate surface properties, surface modi-

fication is an essential step. Surfactants such as CTAB and sodium dodecyl sulfate (SDS) have been used to modify silica particles through physical adsorption [13,18]. Unfortunately, the efficiency of such modifications is often limited. By contrast, chemical modification can effectively improve the surface hydrophobicity of solid particles. Silane coupling agents are widely used as chemical modifying reagents for silica. The dispersibility and stability of silica nanoparticles bonded with 3-methacryloxypropyltrimethoxysilane (KH570) or 3-aminopropyltriethoxysilane (KH550) in several organic solvents have been shown to be improved greatly [19]. It is noted that the agents with different alkyl groups exhibit different functions that influence the application system greatly. Unfortunately, few studies on the effects of alkyl groups on the foam stability have been reported thus far.

The effect of particle size on the foam stability is a topic of disagreement among investigators. Some researchers have speculated that the stability of a liquid film is inversely proportional to particle size [9], whereas some others have suggested that the foam stability is not related to particle size [20]. After all, the levitation behavior of nanoparticles as a foam stabilizer differs completely from that of micrometer-sized particles under the influence of gravity, which favors the foam stability. Nevertheless, the calculation by Binks and Lumsdon [21] shows that the detachment energy associated with escape from the liquid film will become small when the particle size is smaller than 100 nm, which adversely affects the foam stability.

Consequently, in this study, spherical silica nanoparticles were prepared as a solid foam stabilizer in sizes ranging from 100 to 200 nm. To achieve the optimal surface hydrophobicity and foam stabilization, three silane coupling agents were selected with various alkyl chain lengths and structures as foam modifiers. The film stability was evaluated on the basis of both the foam drainage half-life and the expansion viscoelastic modulus of the liquid film. The results of this work were expected to lay a solid foundation for a further practical application of foam systems in the tertiary oil sweeping industry.

2. Experiments

2.1. Materials

SDS (reagent grade) was purchased from Sinopharm Chemical Reagent Co. Ltd., China. Other chemical reagents (analytical grade) were purchased from Beijing Chemical Factory, China.

2.2. Methods

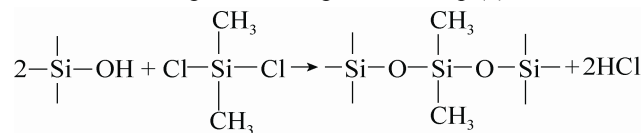
2.2.1. Preparation of silica nanoparticles

Silica nanoparticles were prepared using an improved Stöber method [22]. Briefly, 4.5 mL tetraethylorthosilicate (TEOS) was added to 45.5 mL ethanol, and the resulting mixture was stirred for 10 min; this mixture was referred as solution A hereafter. Additionally, 9 mL ammonia and 16.25 mL ethanol were mixed with 24.75 mL deionized water; the resulting solution was referred as solution B hereafter. Solution B was subsequently quickly poured into solution A and then stirred for 2 h. Finally, the product was collected, washed with ethanol and deionized water at least five times, and dried at 60°C overnight.

2.2.2. Modification of silica nanoparticles

The prepared silica was modified using silane coupling agents with different alkyl chain lengths and structures as dimethyldichlorosilane ((CH₃)₂SiCl₂), 3-methacryloxypropyltrimethoxysilane (KH570), and 3-aminopropyltriethoxysilane (KH550). Their structural formulas are shown in Table 1. The length of the alkyl chains increases in the order as (CH₃)₂SiCl₂ < KH550 < KH570. The (CH₃)₂SiCl₂ contains two CH₃ groups bonded to an Si atom, whereas the alkyl chains of KH550 and KH570 are longer.

In typical process of (CH₃)₂SiCl₂ modification, 2 g nano-SiO₂ was added to 40 mL ethanol solution and sonicated for 10 min at 40°C to obtain a homogeneous suspension. 10 mL ethanol solution containing various mass fractions of (CH₃)₂SiCl₂ (0.01%, 0.03%, 0.05%, 0.07%, and 0.1%) was added dropwise to the suspension. Then, 0.2 mL deionized water was added dropwise into the system. After refluxing for 50 min at 120°C, the resulting solid was collected by centrifugation, washed with ethanol three times, then dried at 60°C overnight. The obtained samples were denoted as *x*(CH₃)₂SiCl@SiO₂, where *x* reflects the mass fraction of (CH₃)₂SiCl₂ added. The chemical reaction during the modification process is expressed as Eq. (1).



(1)

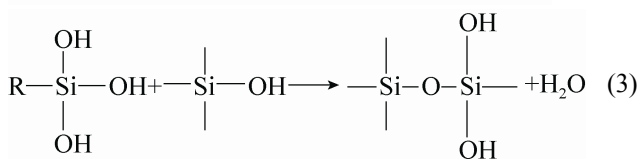
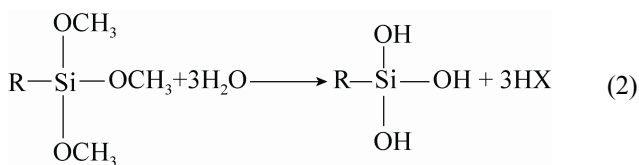
For KH570 modification, 2 g nano-SiO₂ powder was dispersed in a 40-mL mixed solution of ethanol and deionized water (3:1 by volume) by sonication. KH570 with a designed mass fraction (1%, 5%, 10%, 15%, or 20%) was added to the suspension under stirring. Oxalic acid was added dropwise to adjust the suspension pH value of 4–5. After the suspension was refluxed for 2 h at 70°C, the resulting solid was separated, washed, and dried at 60°C. The

obtained samples were denoted as $x\text{KH570@SiO}_2$, where x indicates the mass fraction of KH570 added. The

chemical reaction of KH570 modification is expressed as Eqs. (2) and (3).

Table 1. Structural formulas of the modifiers

Selected modifier	Structural formula
$(\text{CH}_3)_2\text{SiCl}_2$	$\begin{array}{c} \text{Cl} \\ \\ \text{CH}_3 - \text{Si} - \text{CH}_3 \\ \\ \text{Cl} \end{array}$
KH570	$\begin{array}{c} \text{O} \\ \\ \text{H}_2\text{C} = \text{C} - \text{HC} - \text{O} - \text{H}_2\text{C} - \text{Si} - \text{OCH}_3 \\ \qquad \qquad \qquad \qquad \qquad \qquad \\ \text{CH}_3 \qquad \qquad \qquad \text{OCH}_3 \qquad \qquad \qquad \text{OCH}_3 \end{array}$
KH550	$\begin{array}{c} \text{OC}_2\text{H}_5 \\ \\ \text{NH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{Si} - \text{OC}_2\text{H}_5 \\ \\ \text{OC}_2\text{H}_5 \end{array}$



For the KH550 modification, 2 g nano- SiO_2 was dispersed in 40 mL ethanol solution by stirring for 10 min. The KH550 with a designed mass fraction of KH550 (0.02%, 2%, 5%, 10%, or 15%) was then added under stirring. Subsequently, 2 mL deionized water was added dropwise to the system. After being refluxed for 2 h at 80°C , the resulting solid was separated, washed, and dried at 60°C . The obtained samples were denoted as $x\text{KH550@SiO}_2$, where x reflects the mass fraction of KH550. The chemical principle of KH550 modification was similar to that of KH570 modification.

2.2.3. Characterization of silica nanoparticles

Transmission electron microscopy (TEM, TECNAI F-20) was used to observe the morphology of particles. A Fourier transform infrared spectrometer (FTIR, IR-8400S, Shimadzu) with a scanning resolution of 4 cm^{-1} was used to characterize the surface groups of samples. The contact angle was measured using a First Ten Ångströms FTA200 dynamic contact angle measurement system. Each measurement was performed three times to ensure reproducibility.

2.2.4. Foam stability experiments

Foam stability can be defined by static and/or dynamic

stability. The drainage half-life is often used to evaluate static foam stability, which is notably influenced by the film drainage velocity [23]. The expansion viscoelastic modulus is often employed to characterize the dynamic stability with respect to the film interface relaxation process among molecules forming a liquid film, although the method used to determine the expansion viscoelastic modulus differs among different labs [24].

In detail, static foam stability experiments were performed according to the Waring blender method [23]. The dispersions were prepared by mixing 0.03 g silica sample in 100 mL of $8.7 \times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$ SDS solution at room temperature and were subsequently foamed via high-speed stirring in a blender for 60 s (Cole-Parmer, US). The foamability was characterized on the basis of the initial foam volume (V_0), and the foam stability was evaluated on the basis of the drainage half-life, $t_{1/2}$ (i.e., the time consumed when half the volume of the liquid is drained). The expansion modulus (E) of a liquid film was expressed by $E = d\gamma/d\ln A$, where γ and A are the surface tension and surface area of the liquid film, respectively, both of which can be measured using the FTA200 dynamic contact angle measurement system.

3. Results and discussion

3.1. Surface properties of silica nanoparticles

3.1.1. TEM and FTIR analyses

The TEM images of original silica particles synthesized via an improved Stöber method are shown in Fig. 1. The silica particles prepared are spherically shaped, with a diameter of approximately 150–190 nm. Fig. 2 shows the FTIR

spectra of the silica particles. In Fig. 2(a), the characteristic absorption peaks of the original silica at 460 cm^{-1} , 750 cm^{-1} , and $1020\text{--}1200\text{ cm}^{-1}$ are assigned to the bending vibration, asymmetric absorption, and asymmetric stretching absorption of Si–O–Si, respectively. The weak absorption peak at 970 cm^{-1} is attributed to the bending vibration absorption of Si–OH. The broad peak at 3300 cm^{-1} is attributed to the absorption by silanol groups (Si–OH). In addition, the absorption peak at 1640 cm^{-1} may be caused by the bending vibration of H_2O . Compared with the spectrum of silica, that of modified silica exhibits the characteristic peaks of the modifier separately. For example, the peaks at 2900 cm^{-1} and $\sim 1300\text{ cm}^{-1}$, which correspond to $-\text{CH}_3$, appear in the spectrum of silica modified with $(\text{CH}_3)_2\text{SiCl}_2$ in Fig. 2(b). In particular, the peaks assigned to Si–OH ($\sim 970\text{ cm}^{-1}$) almost disappear and the peaks assigned to Si–O–Si (e.g., $\sim 750\text{ cm}^{-1}$) become notably strong, indicating the chemical reaction in Eq. (1) between the surface groups of silica and the modifier. The peaks at 1560 cm^{-1} and 1390 cm^{-1} , which correspond to the bending vibration of N–H and non-vibration of C–H, respectively, in the spectrum of KH550@SiO_2 in Fig. 2(c), suggest the presence of KH550. In the case of KH570@SiO_2 (Fig. 2(d)), the absorption peaks at 1505 cm^{-1} and 2928 cm^{-1} , which correspond to C–C vibrations and $-\text{CH}_3$ and $-\text{CH}_2$ vibrations, respectively, indicate the character of KH570 [25–26]. It was concluded that all three modifiers were successfully grafted onto the surfaces of silica particles.

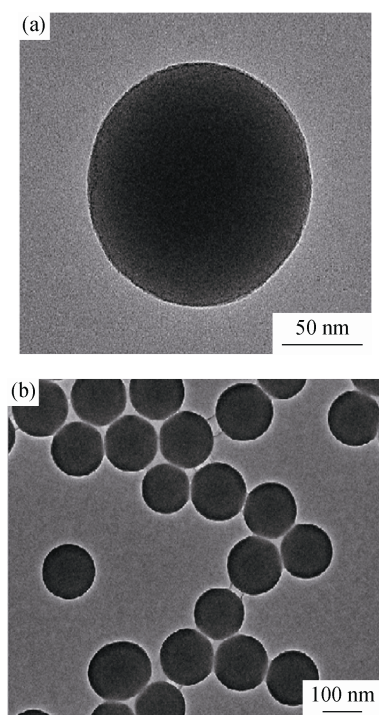


Fig. 1. TEM images of the silica sample.

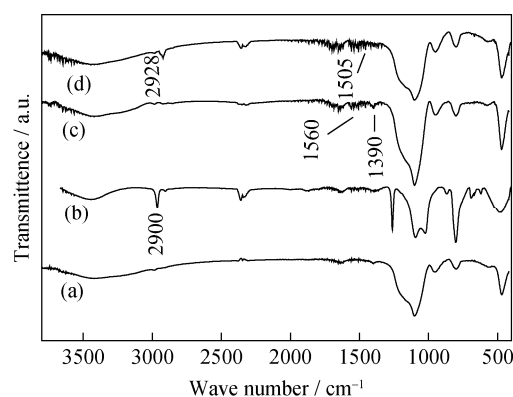


Fig. 2. FTIR spectra of prepared samples: (a) silica; (b) 0.05% $(\text{CH}_3)_2\text{SiCl}_2@SiO_2$; (c) 5% KH550@SiO_2 ; (d) 5% KH570@SiO_2 .

3.1.2. Hydrophobicity analysis

As previously discussed, the organic hydrophobic groups were successfully grafted onto the surfaces of silica particles after modification. This grafting must change the surface hydrophobicity of particles. Fig. 3 shows the changes in contact angles of modified silica particles as functions of modifier content. The contact angles of all of the modified samples clearly increase with increasing content of modifiers. This result indicates that all three modifiers effectively change the surface hydrophobicity of silica samples despite their different modifier dosages. Compared with KH570 and KH550, a relatively small dosage of $(\text{CH}_3)_2\text{SiCl}_2$ can notably increase the contact angle of silica particles, which means that $(\text{CH}_3)_2\text{SiCl}_2$ modification has the highest efficiency in changing the surface hydrophobicity of silica particles, possibly because of its two $-\text{CH}_3$ groups bonded to an Si atom in the molecular structure. Because the $(\text{CH}_3)_2\text{SiCl}_2$ is less hydrophobic than KH550 and KH570, resulting in the greater affinity for silica particles.

3.2. Evaluation of foam stability

3.2.1. Dosage of solid particles

The influence of the solid particles' dosage on foam stability and foam volume is shown in Fig. 4. The drainage half-life first increases, then decreases with the solid dosage, and arrives at the maximum value at 0.03wt% of solid dosage. With increasing content of silica particles, the particles are adsorbed onto the gas–liquid interface to form an orderly stable structure and to increase the strength and viscosity of the interface film, leading to stable foam. However, the excess solid particles can cause aggregation and settling, resulting in the breakage of stable interface film and a decrease in foam stability. The foam volume decreases slightly from 550 to 530 mL. In addition, it was observed that the

experimental results were difficult to reproduce, exhibiting substantial errors (± 20 mL). Therefore, the influence of the solid particles dosage on the foam volume should be neglected. The optimum dosage of solid particles is 0.03wt%.

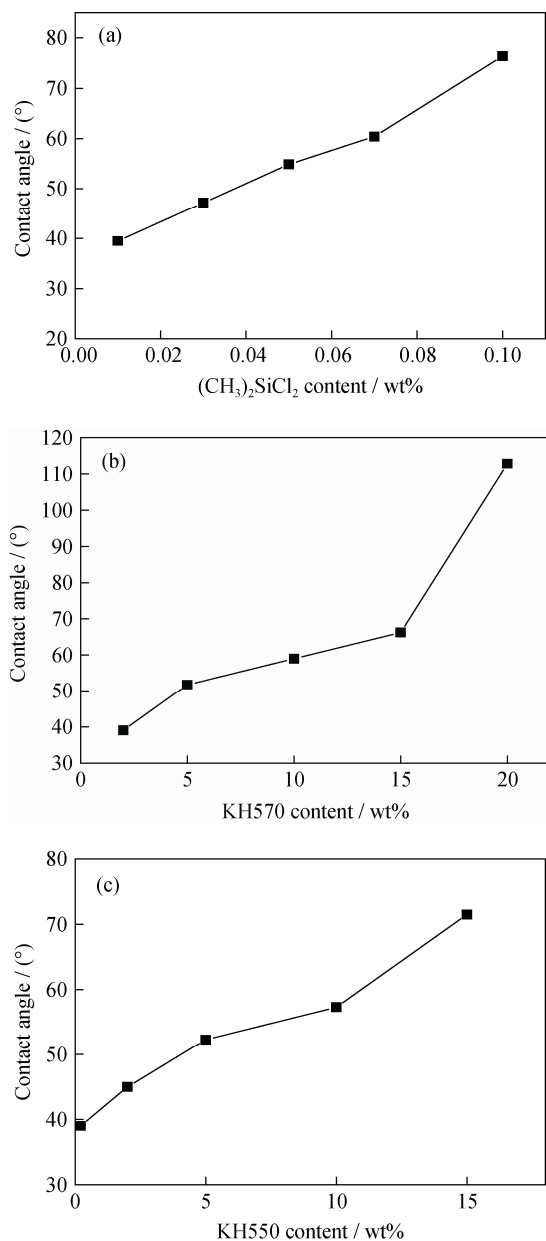


Fig. 3. Contact angle of modified silica particles as a function of modifier content: (a) $(\text{CH}_3)_2\text{SiCl}_2$; (b) KH570; (c) KH550.

3.2.2. Foam stabilization property of modified silica particles

The foam volume and drainage half-life of the systems stabilized by modified silica particles are shown in Fig. 5. The foam volume of each foam system generally shows a decreasing trend with the dosage of modifier; however, the decrease in amplitude can almost be neglected (e.g., 50 mL

for $(\text{CH}_3)_2\text{SiCl}_2@\text{SiO}_2$ samples at the maximum). Therefore, it can be concluded that the solid particles have little influence on the foam volume.

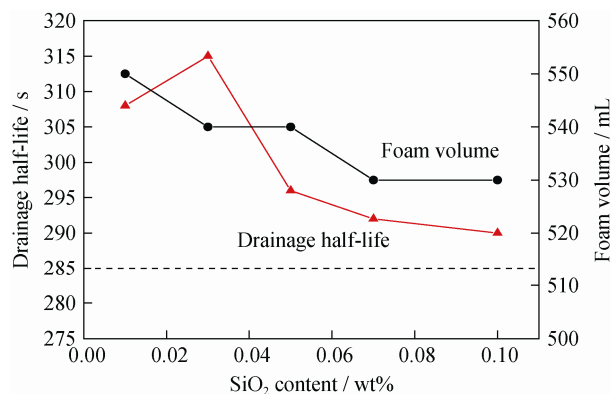


Fig. 4. Stability of a foam system stabilized by $(\text{CH}_3)_2\text{SiCl}_2@\text{SiO}_2$ with different dosages of solid, where the dashed line indicates the drainage half-life of the foam system without the addition of silica particles.

For each modifier, the drainage half-life of the system stabilized by the modified solid particles first increases and then decreases with the dosage of modifier. It reaches a maximum when 0.05wt% $(\text{CH}_3)_2\text{SiCl}_2$, 5wt% KH550, and 5wt% KH570 are used separately. Compared to the corresponding control foam system (the dashed lines in Fig. 5), the drainage half-lives of the foam systems stabilized by modified silica increases a maximum by 27% for $(\text{CH}_3)_2\text{SiCl}_2@\text{SiO}_2$, 11% for KH550@SiO₂, and 11% for KH570@SiO₂, respectively. These results indicated that the modified solid particles increased the foam system stability. Interestingly, all of the maximum foam stabilities were attained when the contact angle of the modified solid particles was in the approximate range from 50° to 55° (54.9°, 53.4°, and 51.9°, as evident in Fig. 3); these values were within or similar to those reported in Ref. [16]. This similarity among contact angles was caused by the synergistic effect of adsorption energy and capillary force among particles. Furthermore, it was noted that the highest drainage half-life occurred in the foam system stabilized by $(\text{CH}_3)_2\text{SiCl}_2@\text{SiO}_2$ and was much higher than those of the systems stabilized by KH550@SiO₂ and KH570@SiO₂ despite their similar hydrophobicities.

The results indicate that the stabilizing foam property of the solid particles not only depends on the surface hydrophobicity but also on the molecular structure of the modifier. Compared to KH550 and KH570, the molecular structure of $(\text{CH}_3)_2\text{SiCl}_2$ differs substantially with respect to the quantity and position of alkyl groups (Table 1). In $(\text{CH}_3)_2\text{SiCl}_2$, two short $-\text{CH}_3$ groups occupy two positions of the tetrahedron centered around Si; by contrast, a single long alkyl group

occupies one position of the tetrahedra in the cases of KH550 and KH570, as shown in Fig. 6. When the modified silica particles were dispersed in the gas–liquid interface formed by SDS and water molecules, the particles modified by $(\text{CH}_3)_2\text{SiCl}_2$ with two $-\text{CH}_3$ groups oriented in two directions could be arranged in a more orderly fashion among the SDS molecules because of the appropriate van der Waals forces between the $-\text{CH}_3$ and the alkyl group of SDS molecules than those modified by the molecules with a single alkyl group, thus resulting in greater foam stability.

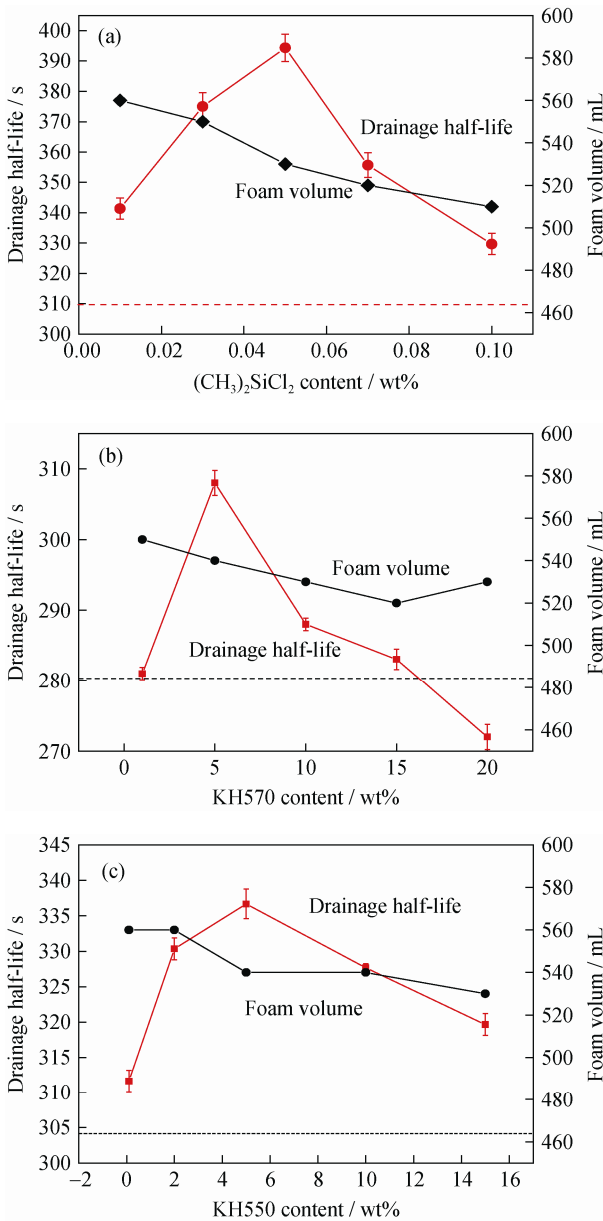


Fig. 5. Foam volume and drainage half-life of the systems stabilized by silica particles: (a) $(\text{CH}_3)_2\text{SiCl}_2@SiO_2$; (b) $\text{KH570}@SiO_2$; (c) $\text{KH550}@SiO_2$. The dashed line indicates the drainage half-life of the foam system without the addition of silica particles.

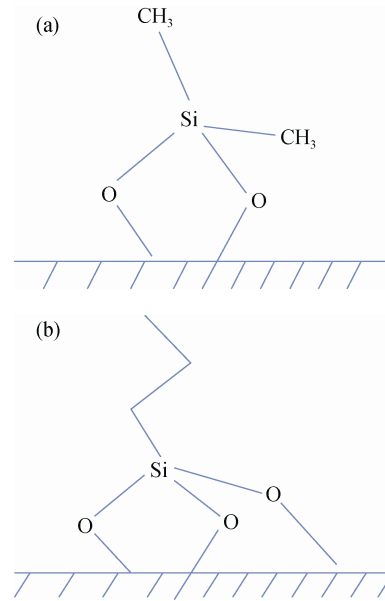


Fig. 6. Schematic structures of modifiers bonded to the surface of silica particles: (a) $(\text{CH}_3)_2\text{SiCl}_2$; (b) KH550 or KH570.

3.2.3. Viscoelasticity of liquid films

The expansion viscoelastic modulus reflects the ability of a film to resist deformation and maintain the original morphology. A film with a high expansion viscoelasticity has the strong self-recovery ability after being disturbed. The changes in drainage half-life and expansion viscoelastic modulus (E) of the foam system stabilized by modified silica particles are shown in Fig. 7. As reported by others [27], the addition of solid particles notably influences the viscoelastic expansion of liquid foams. With increasing modifier dosage, the expansion viscoelastic modulus of the foam system exhibits the same tendency as the drainage half-life, first increasing and then decreasing. Like the drainage half-life, the viscoelastic modulus also reaches a maximum when 0.05wt% $(\text{CH}_3)_2\text{SiCl}_2$, 5wt% KH550, and 5wt% KH570 are used. These results indicated that the optimal content of modified silica particles could effectively improve both the static stability and the dynamic stability of the foam system. As previously noted, the added solid particles firmly adsorbed onto the gas–liquid interface of the foam system to form a closely packed shell structure, and even to form a strong bridge network when silica particles with the optimum surface hydrophobicity were used; this behavior could not only effectively reduce the liquid discharging speed and hinder the bubble coalescence but also improve the self-recovery ability when disturbed. The determined absolute data of expansion viscoelastic modulus were observed to be poor repeatable and differed substantially among different batches and instruments. Consequently, a comparison of the expansion viscoelastic modulus

values for different foam systems was not possible.

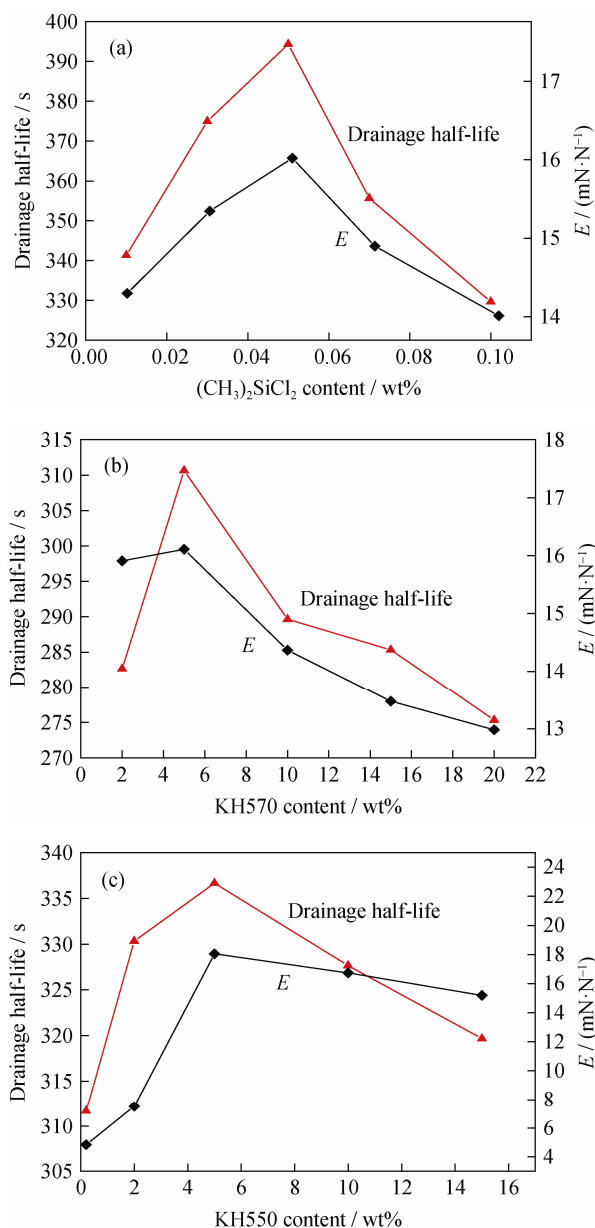


Fig. 7. Drainage half-life and expansion viscoelastic modulus of silica samples: (a) $(\text{CH}_3)_2\text{SiCl}_2@SiO_2$; (b) KH570@SiO₂; (c) KH550@SiO₂.

4. Conclusion

Spherical silica particles with diameters ranging from 150 to 190 nm were prepared and used as a solid foam stabilizer. Three silane coupling agents were selected as modifiers to alter the surface hydrophobicity of the silica particles. FTIR and hydrophobicity analysis results indicate that the modifiers are successfully grafted onto the silica particle surfaces through chemical reactions and effectively improve

the hydrophobicity of silica particles. The surface hydrophobicity of the modified particles plays a key role in improving the foam stability. The foam stability, including the static stability and dynamic stability, is effectively improved when the contact angle of particles is in the approximate range from 50° to 55°. Under the optimum conditions, the drainage half-life of the foam system increases by 27% compared to that of the blank foam system. The molecular structure of the modifier also influences the foam stabilization property of solid particles. Compared with silica particles modified by KH570 and KH550, silica particles modified by $(\text{CH}_3)_2\text{SiCl}_2$ exhibit the excellent performance in foam stabilizing.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21276022) and the China National Petroleum Corporation Innovation Foundation (No. 2012D-5006-0208).

References

- [1] Y.J. Bu, R.Q. Liu, W. Sun, and Y.H. Hu, Synergistic mechanism between SDBS and oleic acid in anionic flotation of rhodochrosite, *Int. J. Miner. Metall. Mater.*, 22(2015), No. 5, p. 447.
- [2] X.T. Zhang, M.H.S. Ismail, F.R.B. Ahmadun, N.B.H. Abdullah, and C. Hee, Hot aerosol fire extinguishing agents and the associated technologies: a review, *Braz. J. Chem. Eng.*, 32(2015), No. 3, p. 707.
- [3] S.F. Turner, S.M. Clarke, A.R. Rennie, P.N. Thirtle, D.J. Cooke, Z.X. Li, and R.K. Thomas, Adsorption of sodium dodecyl sulfate to a polystyrene/water interface studied by neutron reflection and attenuated total reflection infrared spectroscopy, *Langmuir*, 15(1999), p. 1017.
- [4] X. Xu, A. Saeedi, and K. Liu, Laboratory studies on CO₂ foam flooding enhanced by a novel amphiphilic ter-polymer, *J. Pet. Sci. Eng.*, 138(2016), p. 153.
- [5] Q.W. Wang, J.T. Zheng, X.L. Cao, P. Guo, and X.L. Li, Foam capacity in tertiary oil recovery and application in pilot, *J. China Univ. Pet.*, 32(2008), No. 3, p. 93.
- [6] N. Karolina, M. Tomislav, and S. Katarina, Increased hydrocarbon recovery and CO₂ management, a Croatian example, *Environ. Earth Sci.*, 68(2013), No. 4, p. 1187.
- [7] L.P. Wan, Y.F. Meng, and X.D. Zhao, Mechanism study on stability of foam fluid, *J. Xinjiang Pet. Inst.*, 15(2003), No. 1, p. 70.
- [8] X.Q. Dong, D.J. Sun, G.P. Liu, C.B. Cao, and X.R. Jiang, Aqueous foam stabilized by hydrophobically modified cellulose and alkyl polyoxyethyl sulfate complex in the presence and absence of electrolytes, *Colloids Surf. A*, 345(2009), No.

- 1-3, p. 58.
- [9] F.Q. Tang, Z. Xiao, J.A. Tang, and L. Jiang, The effect of SiO₂ particles upon stabilization of foam, *J. Colloid Interface Sci.*, 131(1989), No. 2, p. 498.
- [10] Q. Liu, S.Y. Zhang, D.J. Sun, and J. Xu, Aqueous foams stabilized by hexylamine-modified Laponite particles, *Colloids Surf. A*, 338(2009), No. 1-3, p. 40.
- [11] R.G. Alargova, D.S. Warhadpande, V.N. Paunov, and O.D. Velev, Foam super-stabilization by polymer microrods, *Langmuir*, 20(2004), No. 24, p. 10371.
- [12] S. Nakayama, S. Hamasaki, K. Ueno, M. Mochizuki, S. Yusa, Y. Nakamura, and S. Fujii, Foams stabilized with solid particles carrying stimuli-responsive polymer hairs, *Soft Matter*, 12(2016), p. 4794.
- [13] X.Q. Dong, J. Xu, C.B. Cao, D.J. Sun, and X.R. Jiang, Aqueous foam stabilized by hydrophobically modified silica particles and liquid paraffin droplets, *Colloids Surf. A*, 353(2010), No. 2-3, p. 181.
- [14] B.P. Binks and T.S. Horozov, Aqueous foams stabilized solely by silica nanoparticles, *Angew. Chem. Int. Ed.*, 44(2005), No. 24, p. 3722.
- [15] G. Urbano, I. Lázaro, I. Rodríguez, J.L. Reyes, R. Larios, and R. Cruz, Electrochemical and spectroscopic study of interfacial interactions between chalcopyrite and typical flotation process reagents, *Int. J. Miner. Metall. Mater.*, 23(2016), No. 2, p. 127.
- [16] G. Kaptay, Interfacial criteria for stabilization of liquid foams by solid particles, *Colloids Surf. A*, 230(2003), No. 1-3, p. 67.
- [17] I. Ojea-Jiménez, P. Urbán, F. Barahona, M. Pedroni, R. Capomaccio, G. Cecone, A. Kinsner-Ovaskainen, F. Rossi, and D. Gilliland, Highly flexible platform for tuning surface properties of silica nanoparticles and monitoring their biological interaction, *ACS Appl. Mater. Interfaces*, 8(2016), No. 7, p. 4838.
- [18] B. Qiao, Y. Liang, T.J. Wang, and Y.P. Jiang, Surface modification to produce hydrophobic nano-silica particles using sodium dodecyl sulfate as a modifier, *Appl. Surf. Sci.*, 364(2016), p. 103.
- [19] X.H. Li, Z. Cao, Z.J. Zhang, and H.X. Dang, Surface-modification *in situ* of nano-SiO₂ and its structure and tribological properties, *Appl. Surf. Sci.*, 252(2006), No. 22, p. 7856.
- [20] M. Ru, Z.D. Chang, W.L. Luo, W.J. Li, S.N. Gu, Y.Q. Zhang, H. Qiu, and J.L. Niu, Influence of hydrophobically modified silicon dioxide particles on stability of EOR flooding foam, *J. Chem. Ind. Eng.*, 63(2012), No. 6, p. 1943.
- [21] B.P. Binks and S.O. Lumsdon, Influence of particle wettability on the type and stability of surfactant-free emulsions, *Langmuir*, 16(2000), No. 23, p. 8622.
- [22] K. Do Kim and H.T. Kim, Formation of silica nanoparticles by hydrolysis of TEOS using a mixed semi-batch/batch method, *J. Sol-Gel Sci. Technol.*, 25(2002), No. 3, p. 183.
- [23] Z.W. Guo, C.X. Xu, Y. Lu, and L.Z. Zhou, Foamability and stability of foam and means of evaluating, *Chem. Eng.*, 127(2006), No. 4, p. 51.
- [24] D. Arabadzhieva, E. Mileva, P. Tchoukov, R. Miller, F. Ravera, and L. Liggieri, Adsorption layer properties and foam film drainage of aqueous solutions of tetraethyleneglycol monododecyl ether, *Colloids Surf. A*, 392(2011), No. 1, p. 233.
- [25] D.L. Yi, Z.H. Ouyang, L. Wu, and X.R. Qin, Surface modification of nano-SiO₂ and its application in butyl rubber, *J. Wuhan Univ. Sci. Technol.*, 30(2007), No. 6, p. 640.
- [26] Q. Zhang, C. Bi, Y.G. Li, M.F. Zhu, and H.Z. Wang, Study on surface modification of the SiO₂ nanoparticles and dispersion, *New Chem. Mater.*, 36(2008), No. 5, p. 41.
- [27] H.R. Wang, Y. Gong, W.C. Lu, and B.L. Chen, Influence of nano-SiO₂ on dilational viscoelasticity of liquid/air interface of cetyltrimethyl ammonium bromide, *Appl. Surf. Sci.*, 254(2008), No. 11, p. 3380.