

Long-Term Thermal Stability of Ionic Surfactants for Improving Oil Production at High-Salinity High-Temperature Conditions

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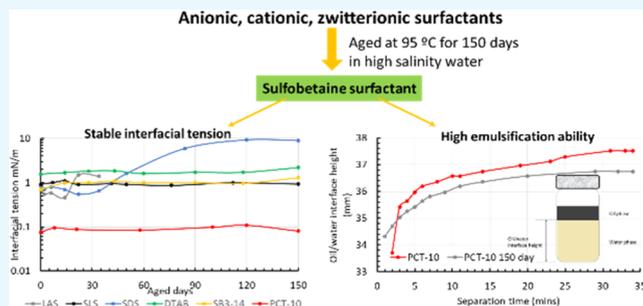


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ABSTRACT: Surfactants with stable chemical structures and robust ability are required to lower interfacial tension and stabilize emulsions for successful chemical injection applications. This work selected six surfactants, dodecyl carboxylic sodium (LAS), dodecyl sulfonate dodecyl sodium (SLS), dodecyl sulfate sodium (SDS), dodecyltrimethylammonium bromide (DTAB), 3-(*N,N*-dimethylmyristylammonio) propanesulfonate (SB3-14) and a sulfobetaine formulation (PCT-10), and systematically investigated the ionic-type effects on thermal stability at 95 °C for 150 days in high-salinity water (total dissolved solids (TDS) = 57,600 ppm). With characterizations of aged samples performed through a spinning drop tensiometer, high-performance liquid chromatography, and infrared spectroscopy, it can be seen that the long-term stability sequence of ionic surfactants in solutions is sulfobetaine \approx quaternary ammonium > sulfonate > sulfate > carboxylate. The carboxylate possibly precipitates out from the solution in the acid form, and the sulfonate and sulfate decompositions are due to the hydrolysis of the anionic head, forming alcohol and $\text{NaHSO}_3/\text{NaHSO}_4$. Obvious decomposition of sulfobetaine and quaternary ammonium was not observed, but these molecules might suffer the elimination of the ionic head, forming the corresponding alkene and amine. The results also show that the dissolved oxygen in the solution preparation significantly sped up the degradation of sulfonates. At last, the emulsion stability tests of crude oil in surfactant solutions showed that sulfobetaine surfactants retained the highest emulsifying ability after thermal aging and thus are promising candidates for long-term chemical injection in high-temperature high-salinity reservoirs.



1. INTRODUCTION

Surfactant-mediated chemical injection is regarded as an effective technique to produce additional oil from developed reservoirs.^{1–3} This technology relies on surfactants to lower the interfacial tension (IFT) between the oil and the injected chemical solutions and emulsify oil to mobilize oil droplets.^{4–6} Depending on the selected chemical injection strategy and reservoir conditions, the injected surfactants might encounter very challenging conditions in terms of high temperature and high salinity in the reservoir and remain for a few months to several years. These factors could induce the decomposition of surfactants, leading to the increase of IFT or a low efficiency to emulsify oil. Therefore, the implementation of a successful chemical injection requires the thermal stability of the selected surfactant over an extended period of time.⁷ Long-term stability tests must be considered in the screening of suitable surfactants, especially for high-temperature and high-salinity (HTHS) reservoirs.^{8–10}

In previous works, the stability affected by temperature and salinity, as well as the different anionic head groups (carboxylate, sulfonate, sulfate etc.) and the functional groups on the acryl chains, was systematically investigated by evaluating the ability to lower the IFT between the water phase and the oil phase, measuring the concentration changes using high-performance

liquid chromatography (HPLC), and characterizing chemical structure alterations through nuclear magnetic resonance (NMR) and infrared spectroscopy (IR) analyses.^{11–13} Regarding the effects of temperature and salinity on thermal stability, Handy et al. reported petroleum sulfonate with a half-life of 11 days at 180 °C but of 33 years at 93 °C by extrapolation when surfactants were prepared in water.¹⁴ In addition, Angstadt et al. also highlighted the excellent stability of linear alkyl benzenesulfonate for temperatures up to 300 °C during steam injection in low-salinity conditions.¹⁵ Under high-salinity conditions, Hocine et al. reported the degradation of sulfates and sulfonates up to 120 °C in months.^{16,17} Regarding the thermal stability of types of surfactants, the concluding results showed that alkyl benzenesulfonate was superior to olefin sulfonate and petroleum sulfonate, which were more robust to temperature than sulfate surfactants. The degradation mecha-

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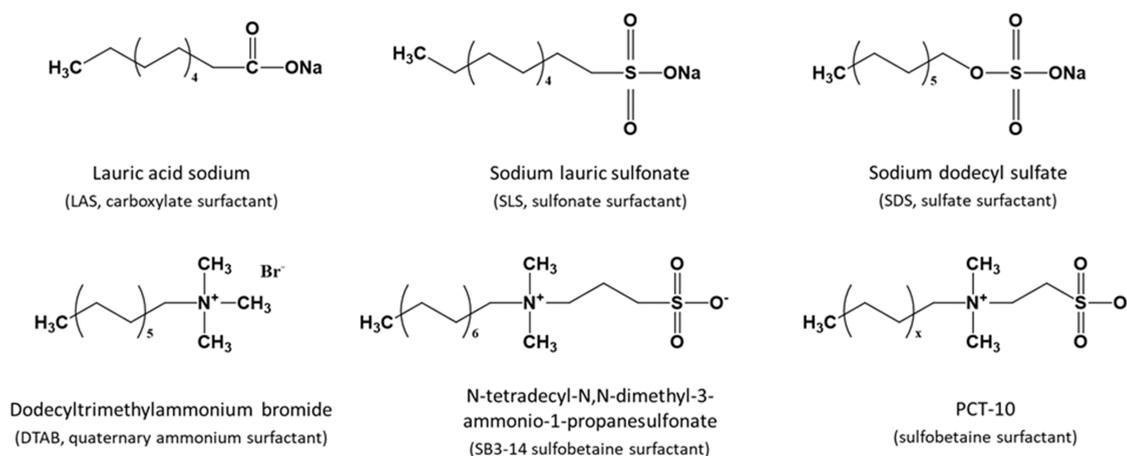


Figure 1. Chemical structures of the selected anionic, cationic, and zwitterionic surfactants.

nism includes the loss of sulfonate or sulfate function by hydrolysis in an acidic or alkaline media,^{18,19} along with oxidative attacks on the side alkyl chain when exposed to oxygen.²⁰ The prior art has clearly explained the stability or degradation of anionic surfactants, taking into account the influence of the side-chain functional group as well.

In the meantime, to address the challenges in severe reservoir conditions, more and more cationic and zwitterionic surfactants are synthesized and applied in chemical injection operations.^{21–25} These surfactants are considered more thermally stable than anionic surfactants; thus, they lack comprehensive investigations on concentrations or chemical structures during long-term thermal aging.

Therefore, this work focuses on a fundamental thermal stability study using surfactants with similar acryl hydrophobic chains (12–14) but various head groups (carboxylate, sulfonate, sulfate, quaternary ammonium, and sulfobetaine). These surfactants are prepared in high-salinity water (HSW) or deionized water, aged for 150 days at 95 °C, and characterized by a spinning drop tensiometer, high-performance liquid chromatography (HPLC), and infrared spectroscopy (IR). Besides, the emulsification abilities of nonaged and 150-day-aged surfactants were carefully compared. By elucidating the degradation mechanism of different ionic surfactants, the results presented in this work offer insights into surfactant selection based on thermal chemical stability and emulsion stabilizing ability.

2. MATERIALS AND METHODS

2.1. Chemicals. Anionic surfactants dodecyl carboxylic sodium (LAS), sodium dodecyl sulfate (SDS), and sodium dodecyl sulfonate (SLS), cationic surfactant dodecyltrimethylammonium bromide (DTAB), and zwitterionic surfactant 3-(*N,N*-dimethylmyristylammonio) propanesulfonate (SB3–14) with 98% purity were purchased from Sinopharm (Beijing). The sulfobetaine surfactant formulation PCT-10 with an activity content of about 30% is from Oilchem. The chemical structures of all of the surfactants are presented in Figure 1. NaCl, CaCl₂·2HO, MgCl₂·6H₂O, NaHCO₃, and Na₂SO₄ of analytical grade were obtained from Sinopharm (Beijing) for the preparation of HSW with the composition shown in Table 1. The composition and salinity of water are based on field data. The prepared high-salinity water was heated at 95 °C for 2 weeks and filtered through a 0.45 μm membrane before being used for surfactant solution preparation. This ensures no salts precipitate to

Table 1. Composition of High-Salinity Water (HSW, TDS = 57,600 ppm)

ions	Na ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻	HCO ₃ ⁻
ion amount, ppm	18,300	650	2110	4290	32,200	120

interfere with the stability of surfactant solutions. The surfactants are dissolved in HSW or deionized water, respectively, and the resultant concentrations are 0.2%. It should be noted that LAS and SLS cannot dissolve in HSW at room temperature, and the solutions are prepared in NaCl with the same TDS at 40 °C. Crude oil used in emulsifying tests is a degassed and dehydrated light oil from a carbonate reservoir. The viscosity of the oil was 2 cP at 90 °C.

2.2. Long-Term Stability Tests. The long-term thermal aging experiments were conducted under anaerobic conditions. To remove oxygen, HSW or DI water was purged with nitrogen for half an hour in a glovebox (O₂ < 1 ppm in air). Then, water was added into weighed surfactant solids and stirred until the solids were completely dissolved. After 0.2% surfactant solutions were prepared, they were separated as 25 mL surfactant solutions in a 50 mL penicillin bottle. The bottles were carefully sealed with compatible rubber caps in a glovebox to prevent water loss. All of the samples were incubated at 95 °C in an oven for a certain time (from 0 to 150 days). To investigate oxygen influences, surfactant solutions of the reference group were prepared in ambient conditions. Then, the samples were separated in penicillin bottles and sealed for aging in an oven.

2.3. High-Temperature Surface Tension Measurements. A spinning drop tensiometer (Kruss, Germany) was used to measure the interfacial tension between air and surfactant solutions at 95 °C to present the surface tension at high temperatures. In the experiment, an air bubble is injected into a spinning tube filled with surfactant solutions and the bubble shape is recorded at a spinning speed of 5000 rpm. The initial volume of the air bubble was as small as <0.1 μL, which further expanded as the temperature increased. The test time was longer than 15 min after reaching 95 °C, which was continued until the volume and shape of the air bubble no longer changed. Additionally, the measurements were conducted three times, and the error bars shown in the figures were calculated based on deviation.

2.4. High-Temperature Interfacial Tension (IFT) Measurements. The IFT between crude oil and surfactant solutions was also measured at 95 °C using the spinning drop tensiometer

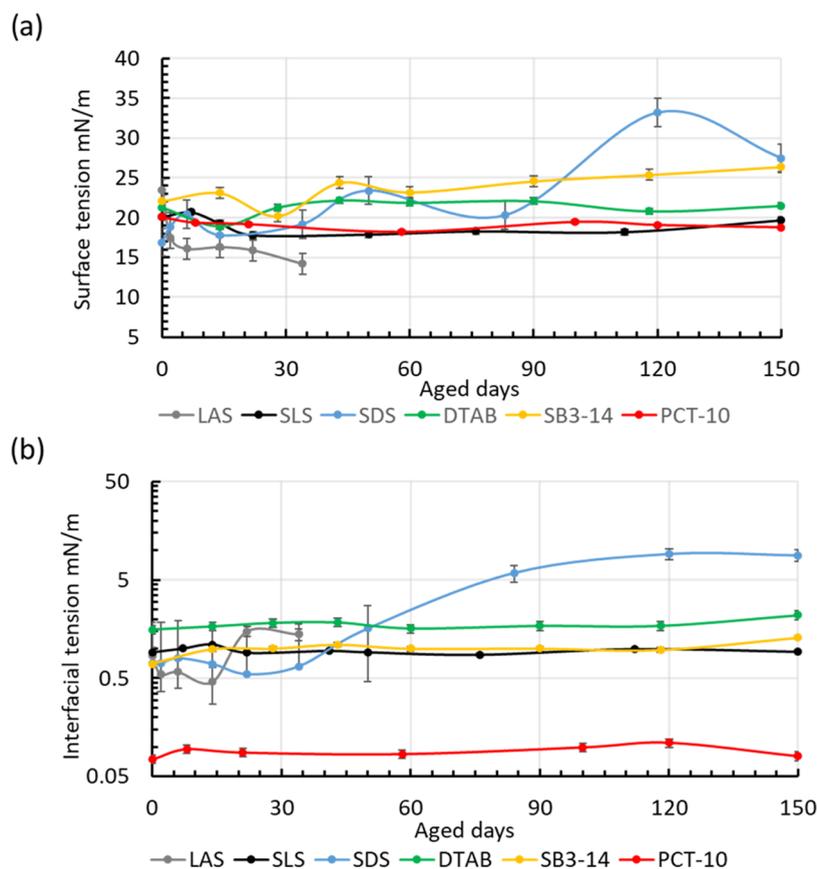


Figure 2. Surface tension (a) and interfacial tension (b) of six surfactants in HSW at 95 °C after thermal aging for different days. The error bars present the deviation of three measurements.

(Kruss, Germany). The experiment operation was similar to surface tension measurements, only that a droplet of 0.2–0.3 μL of oil instead of an air bubble was injected into surfactant solutions.²⁶ Moreover, the measurements were conducted three times, and the error bars shown in the figures were calculated based on deviation.

2.5. Infrared (IR) Spectroscopy Analysis. The aged samples prepared in DI water were characterized by infrared spectroscopy. The 1.5 mL solution samples were freeze-dried for 72 h. The dried solids of surfactants were mixed with KBr to prepare the sample disks, which were then characterized using a Nicolet iS10 FTIR spectrophotometer (Thermo). Sixteen coadded spectra were recorded for each sample at a resolution of 4 cm^{-1} , in the wavenumber range of 500–4000 cm^{-1} . The collected spectra were all processed with baseline adjustment in the OMNIC 7.3.

2.6. High-Performance Liquid Chromatography (HPLC) Analysis. A Shimadzu LC-20A HPLC system was used for characterization of surfactants and determination of the concentrations. The equipment was gradient-programmable and coupled with a surfactant column (25 $\text{cm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$, Thermo) and an evaporative light scattering detector (ELSD). The organic mobile phase was 100% acetonitrile and the water mobile phase was 5% acetonitrile in water with 100 mM ammonium acetate. For the analysis of SLS, the samples were heated to 60 °C and diluted by methanol at a 1:1 volume ratio to prevent precipitation in the analysis process.

2.7. Emulsion Stability Analysis. To prepare the emulsion solutions, 0.2% surfactant solutions in HSW were mixed with oil at a volumetric ratio of 9:1 in glass bottles (total volume of 20

mL) in the first place and then stirred at 5000 rpm for 2 min by an IKEA homogenator for emulsification. Then, the emulsified samples were characterized with an optical solution stability analyzer (DataPhysics MS 20) at 90 °C for a certain time. The backscattering curve of the solutions was recorded. At the interface of oil and water, an abrupt increase of backscattering light was observed, and the height of the oil/water interface to the sample bottle bottom was recorded. With the rupture of emulsion and oil moving to the upper phase, the oil/water interface height will increase to a plateau until the two phases are completely separated. By depicting the oil/water interface height versus time, the stability of the emulsion versus time was determined.

3. RESULTS AND DISCUSSIONS

3.1. Long-Term Thermal Stability of Surfactant Solutions in High-Salinity Water. Figure 2a,b presents the surface tension and IFT of six surfactants with crude oil at 95 °C after aging in HSW separately. We have presented the surface tension of SDS, DTAB, and SB3–14 in deionized water and HSW by the plate method and the spinning drop method, respectively, in Table S1 (Supporting Information). The results showed that the surface tension value obtained by the spinning drop method was lower than the value obtained by the plate method. However, the relative relationships between the surfactants were similar compared to the plate method result. Although the surface tension values could also be relatively low at high temperatures, the results can still indicate a change in the surface tension of aged surfactants measured under the same condition. The results summarized in Tables S1 and S2 show

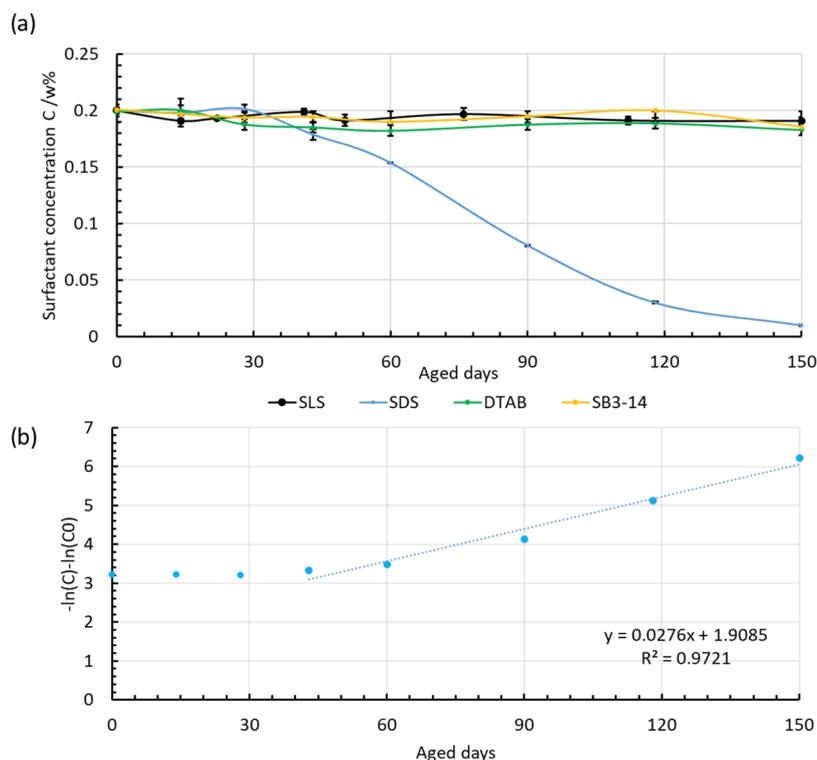


Figure 3. (a) Concentrations of SLS (dark line), SDS (blue line), DTAB (green line), and SB3–14 (yellow line) in HSW after thermal aging. (b) $-\ln(C) - \ln(C_0)$ versus time of SDS. The error bars present three measurements.

Table 2. Summary of Thermal Stabilities of Surfactants

surfactants	references	thermal stability
petroleum sulfonate and sodium dodecylbenzene sulfonate	Handy et al. (ref No. 14)	half-life of the most stable petroleum sulfonate was 11 days at 180 °C and over 33 years at 93 °C in water
alkyl aryl sulfonates (AAS)	Angstadt et al. (ref No. 15)	some are stable over 10 days or months at pH = 7 up to 300 °C when prepared in water
α olefin sulfonate (AOS) and AAS	Cuenca et al., SPE-170129-MS (ref No. 30) Maini et al., SPE 13572 (ref No. 18)	AOS with chain lengths varying from C ₁₂ to C ₁₈ and AAS were stable for up to 1 week up to 240 °C when prepared in water ³⁰ most displayed half-life over 100 days at 200 °C and less than 10 days at 300 °C (prepared in water); alkyl benzene sulfonates (ABS) were superior to AOS, which were better than petroleum sulfonate
alkyl glyceryl ether sulfonate (AGES)	Hocine et al., IPTC-18974-MS, SPE-190361-MS (refs No. 16, 17)	olefin sulfonates were stable at room temperature but decomposed at 100 °C in 3 months; ABS were more stable than OS, which were stable over 1 year at 100 °C in deionized water
alkyl ether sulfates	Hocine et al., IPTC-18974-MS, SPE-190361-MS (refs No. 16, 17)	stable at 80 °C in 24 days and over 1 year at 100 °C in deionized water a poor stability at >100 °C in deionized water as the active contents degraded in days, but they degraded in months in an alkaline buffer
alkyl alkoxy carboxylate	Adkins et al. (ref No. 8)	the surfactants presented stable phase behavior over 400 days at 100 °C when salinity was up to 58,000 ppm
alkyl carboxylate	current work	not stable over 30 days at 95 °C in deionized water and high-salinity water (TDS > 50,000 ppm)
alkyl sulfonate	current work	almost stable in 150 days at 95 °C in high-salinity water
alkyl sulfate	current work	hydrolysis at 95 °C aging in deionized water and high-salinity water
quaternary ammonium surfactant, betaine-type zwitterionic surfactant	current work	almost stable in 150 days at 95 °C in deionized water and high-salinity water

that the surface tension decreased at high temperatures for the measured surfactants. This is possibly because the cohesive forces decrease with an increase of molecular thermal activity. However, generally, the influence of temperature on IFT is complex and depends on surfactant structures, oil properties, and some other factors.^{27–29} The results in Figure 2a show that the surface tension of SLS and PCT-10 was stable in the 150-day aging period. The surface tension of DTAB fluctuated around an average value but did not change much. The surface tension of

SB3–14 increased slightly with initial values of 22.1 and 26.5 mN/m at 150 days, not an obvious change considering the system errors. In the case of IFT with crude oil, the values of the SLS, DTAB, SB3–14, and PCT-10 surfactant solutions were very stable in 150 days of aging. Thus, the four surfactants were mostly thermally stable in the long-term aging tests according to surface behaviors. The LAS solution became turbid, indicating the form of precipitates after 30 days. The surface tension and IFT were not recorded.

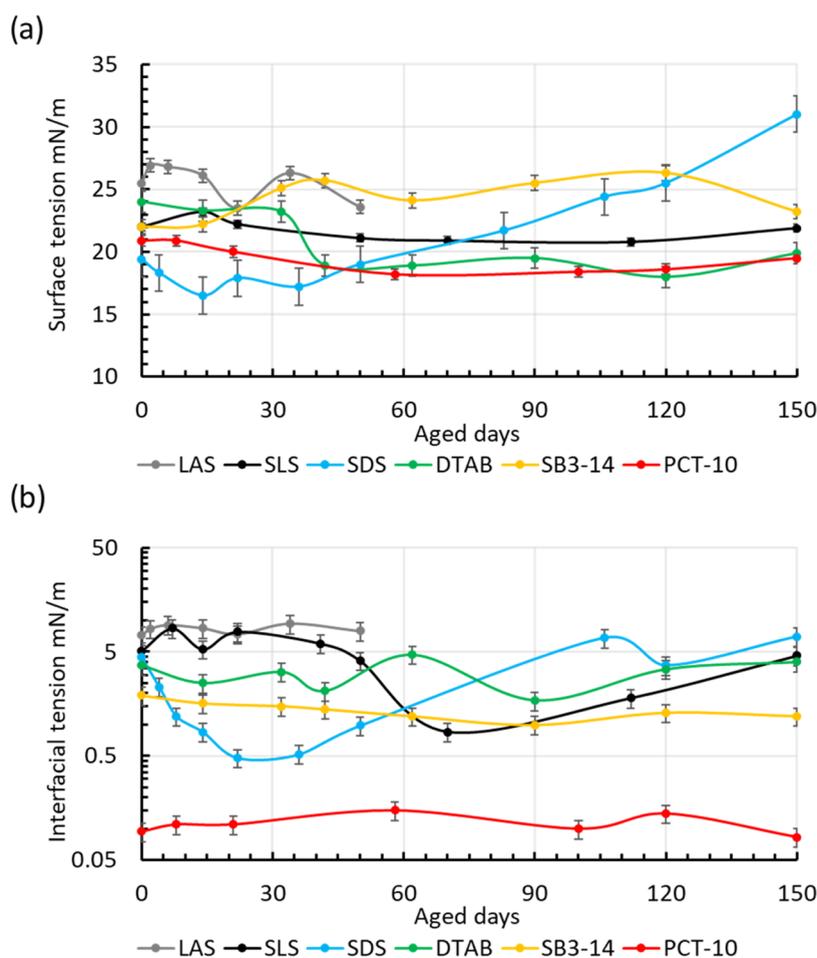


Figure 4. Surface tensions (a) and interfacial tensions (b) of six surfactants in deionized water at 95 °C after thermal aging for different days. The error bars present three measurements.

On the other hand, the surface tension of SDS increased sharply from 16.9 to 27.5 mN/m in 150 days. The IFT of SDS in HSW decreased from 10^0 mN/m to 10^{-1} mN/m in the first 22 days and started to increase until the value was 10^1 mN/m after 80 days of aging. One possible explanation is that, in the initial decomposition stage, the small amounts of degraded fragments cause the decrease of IFT as impurities. With thermal decomposition for longer aging days, the active surfactant concentration decreased, which led to the increase of IFT.

To confirm the stability, the concentrations of SLS, SDS, DTAB, and SB3-14 in HSW in 150 days of aging were calculated based on HPLC peak intensities (Figure 3). It can be seen that the concentration of SDS started to decrease after a month of aging. After 150 days, the remaining concentration was only 0.01%, indicating more than 90% of the surfactants had decomposed, causing the increase of surface tension and IFT. At the same time, the concentrations of SLS, DTAB, and SB3-14 decreased less than 10%. Figure 3b presents the $-\ln(C) - \ln(C_0)$ versus time of SDS, where C is the surfactant concentration at a specific time and C_0 is the initial surfactant concentration before aging. It shows that the decomposition of SDS is a first-order reaction following the equation $kt = -\ln(C) - \ln(C_0)$ after 40 days (k is the reaction rate constant and t is the aging time).

Therefore, in HSW, the sulfonate, quaternary ammonium, and sulfobetaine surfactants are more stable than the carboxylate and sulfate surfactants. We have summarized part of the previous

research and compared the current results with those in Table 2, both demonstrating the long-term instability of sulfate. Moreover, sulfonate is much more stable at around 100 °C than sulfate, which is consistent with Hocine's result.

3.2. Long-Term Thermal Stability of Surfactant Solutions in Deionized Water. Figure 4a,b presents the surface tension and IFT of the six surfactants in deionized water after aging from 0 to 150 days. Usually, the surface tension and IFT decrease with higher salinity (Tables S1 and S2) since (1) the CMC usually decreases under higher salinity; (2) the limited hydration state surfactants in high-salinity solutions make the molecules inclined to aggregate at the interface; and (3) the weakened charge repulsion of ionic surfactants in salt solutions leads to a closer-packed pattern at the interface.²⁷ In our study, the selected surfactants LAS, SLS, SDS, and DTAB followed the general trend, while the surface tension and IFT differences of SB3-14 and PCT-10 in deionized water and HSW at high temperatures were not so obvious. (Table S2) These zwitterionic surfactants could possibly have a relatively close-packed pattern due to charge attraction. The instability of LAS is due to the solution turbidity of LAS after 50 days, which is longer than in HSW. As for SDS, the trends in surface tension and IFT in water were similar to those in HSW. The surface tension increased from 19.4 to 31.0 mN/m. The IFT decreased in the first 30 days and then started to increase from 0.48 mN/m (lowest at 22 days) to 7.0 mN/m at 150 days. In the case of SLS too, a decrease of IFT was observed in the first 60 days, followed

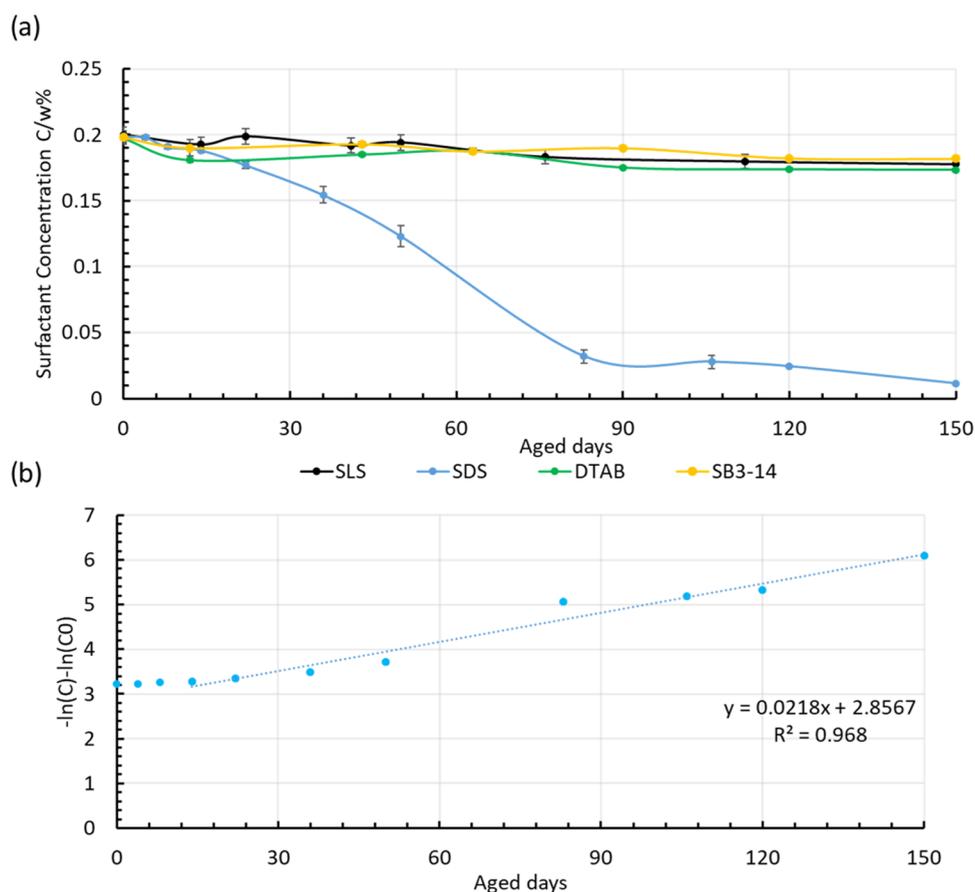


Figure 5. (a) Concentrations of SLS (dark line), SDS (blue line), DTAB (green line), and SB3-14 (yellow line) in deionized water after thermal aging. (b) $-\ln(C) - \ln(C_0)$ versus time of SDS. The error bars present three measurements.

by a slow increase. Different from the results in HSW, these results indicated a slight degradation of SLS in deionized water at high temperatures. As for DTAB, SB3-14, and PCT-10, the conditions of surface tension and IFT did not obviously change, similar to those in HSW.

The concentrations of the four surfactant solutions in deionized water presented a similar trend as that in HSW (Figure 5a), but the remaining concentration of SLS in deionized water at 150 days was about 0.18%, slightly lower than that in HSW (0.19% in Figure 3). This is consistent with surface tension and IFT results. As for SDS, more than 90% of the molecules decomposed and caused an increase in surface tension and IFT. The line of $-\ln(C) - \ln(C_0)$ versus time in Figure 5b shows that the decomposition of SDS also followed a first-order reaction. The reaction rate constant is 0.0218, similar to that of 0.0276 in HSW. However, the degradation starting point was 14 days, earlier than the 40 days for HSW. The delay is possibly because HSW is more alkaline and not favorable for the hydrolysis reaction.^{18,19}

Therefore, the long-term stability sequence of surfactant solutions is sulfobetaine \approx quaternary ammonium > sulfonate > sulfate > carboxylate in water.

3.3. IR Analysis of Surfactants. Since similar results were found for the surface properties and concentrations of surfactant solutions after thermal aging in HSW and deionized water, IR analysis performed on the aged surfactant samples in deionized water helped present the chemical structure alteration in HSW. Samples in HSW were not analyzed because the residual salts in the dried solids severely interfered with the IR spectra.

Figure 6a–f presents the IR spectra of LAS, SLS, SDS, DTAB, SB3-14, and PCT-10 before and after aging at 150 days, respectively. In the case of LAS, the $-\text{COO}^-$ groups presented similar characteristic peaks around 1500 and 2500 cm^{-1} for the nonaged, 34-day-aged, and 150-day-aged samples. The increased envelope at 900 cm^{-1} was possibly due to the $-\text{O}-\text{H}$ bending vibration of the carboxylic group. The nonaged SLS in Figure 6b clearly shows the couples of absorption peaks at 1066, 1169, 1173, and 1468 cm^{-1} , representing the $-\text{S}=\text{O}$ stretching vibration of sulfonate groups.³¹ Compared to the 150-day-aged lines, the peaks at 1169 and 1173 cm^{-1} became a big envelope with some spikes. For the sulfate group in SDS in Figure 6c, the $-\text{S}=\text{O}$ stretching vibration peaks moved to 1080, 1206, 1267, and 1488 cm^{-1} , respectively, slightly higher than those in the sulfonate group. However, after 83 days of aging, the 1080 cm^{-1} peak disappeared. Besides, the peaks at 1206 and 1267 cm^{-1} could not be clearly identified. After 150 days of aging, the peaks turned into big envelopes, which could be attributed to the $-\text{S}=\text{O}$ vibration of NaHSO_4 and the $-\text{C}-\text{O}$ vibration of the formed alcohol. The IR spectra of both nonaged and 150-day-aged DTAB in Figure 6d clearly presented $-\text{N}-\text{H}$ stretching around 2900 cm^{-1} , $-\text{N}-\text{H}$ bending around 1500 cm^{-1} , and $-\text{C}-\text{N}$ stretching around 900 cm^{-1} . As for SB3-14, the IR results (Figure 6e) presented the characteristic vibration of the quaternary amine and sulfonate. Still, no obvious surfactant decomposition was observed except for the very slight increase of the peak at 1780 cm^{-1} , possibly representing the $-\text{C}=\text{C}$ vibration. The spectra of PCT-10 (Figure 6f) also showed the stability of the sulfobetaine component after thermal aging. The

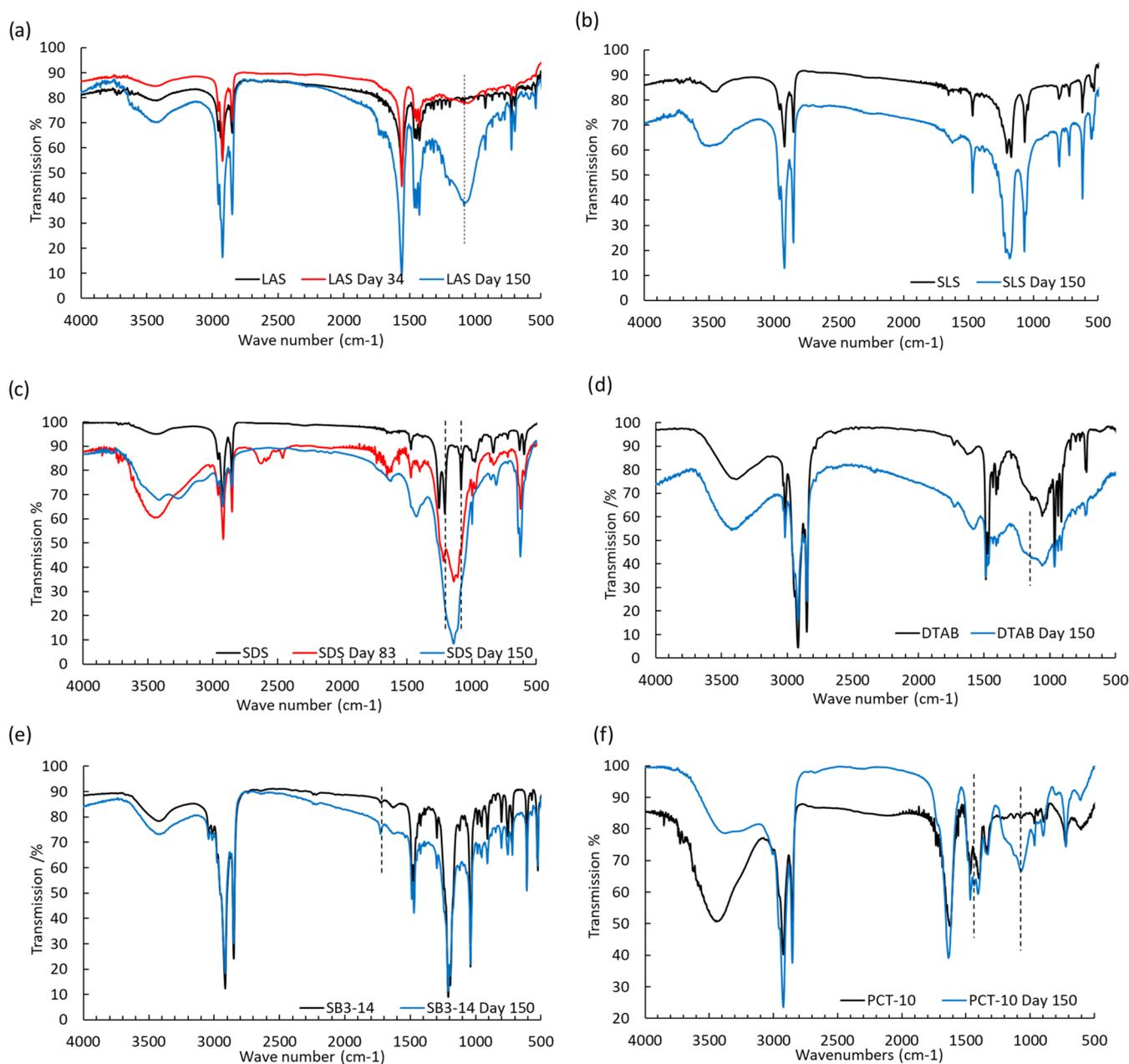


Figure 6. IR spectra of dried surfactant solution samples before and after aging for 150 days: (a) LAS, (b) SLS, (c) SDS, (d) DTAB, (e) SB3–14, and (f) PCT-10.

newly formed peaks may be contributed by cosurfactants in the formulation.

3.4. Chemical Basis of Degradation. With the results from surface properties, HPLC, and IR, we tried to elucidate the degradation mechanism of different types of surfactants, with the chemical equations shown in Figure 7. For the carboxylate surfactant LAS, the molecules presented the highest thermal tolerance in the solid state by the TGA test (Figure S1 in the Supporting Information). However, the pH value of 8.48 for the LAS solutions demonstrates the hydrolysis of the lauric group into lauric acid (Table S4 in the Supporting Information). Moreover, previous studies have reported the hydrolysis of sodium laurate to lauric acid, which then transfers to the oil phase.^{32,33} Since the solubility of lauric acid is ~ 83 mg/L in water at 100 °C, and no degradation of $-\text{COO}^-$ was observed

using IR, there is a possibility that the precipitates were lauric acid.³⁴ High temperatures could facilitate the process.

The decomposition of sulfonate is possibly induced by the hydrolysis of the headgroup, presented in Figure 7. The envelope could be attributed to the $-\text{S}=\text{O}$ vibration of the undecomposed sulfonate group, the $-\text{S}=\text{O}$ vibration of NaHSO_3 , and the $-\text{C}-\text{O}$ stretching vibration of the formed alcohol. In the hydrolysis of the sulfate group, the sulfur is displaced by hydrogen in water and the sulfate is hydrolyzed into the corresponding alcohol and NaHSO_4 .³⁵ The pH values of SDS in HSW before and after aging were 7.36 and 3.41, respectively, consistent with the degradation equation. Besides, this energy barrier of the reaction is lower than the hydrolysis of sulfonate. The IR results did not present a clear degradation clue of DTAB and SB3–14. From previous reports, it can be seen that the theoretical decomposition of quaternary ammonium

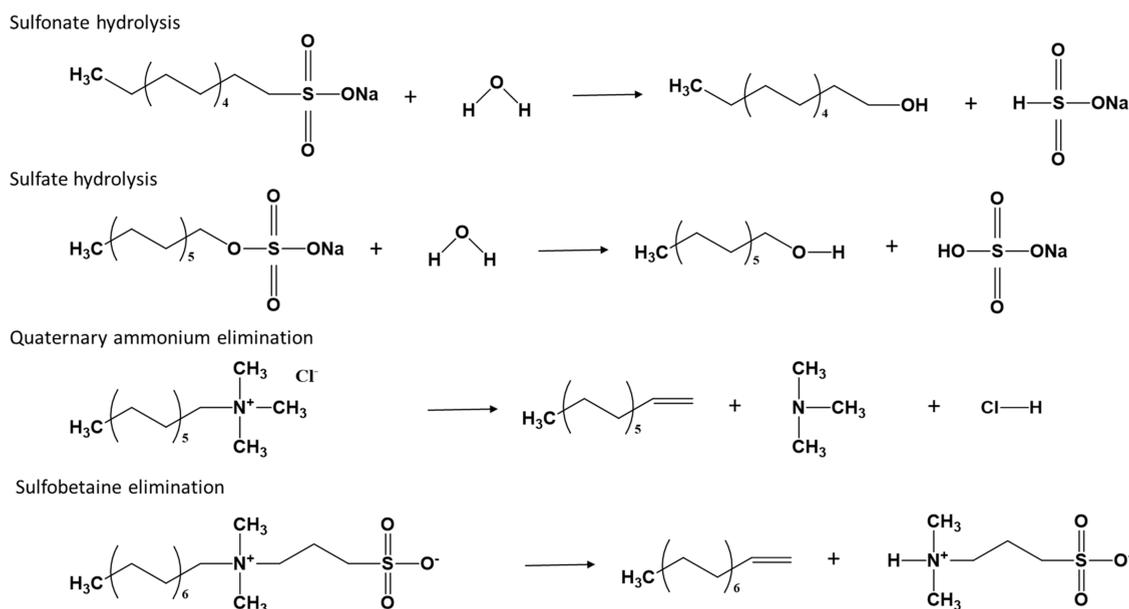


Figure 7. Chemical equations of degradation of SLS, SDS, DTAB, and SB3–14.

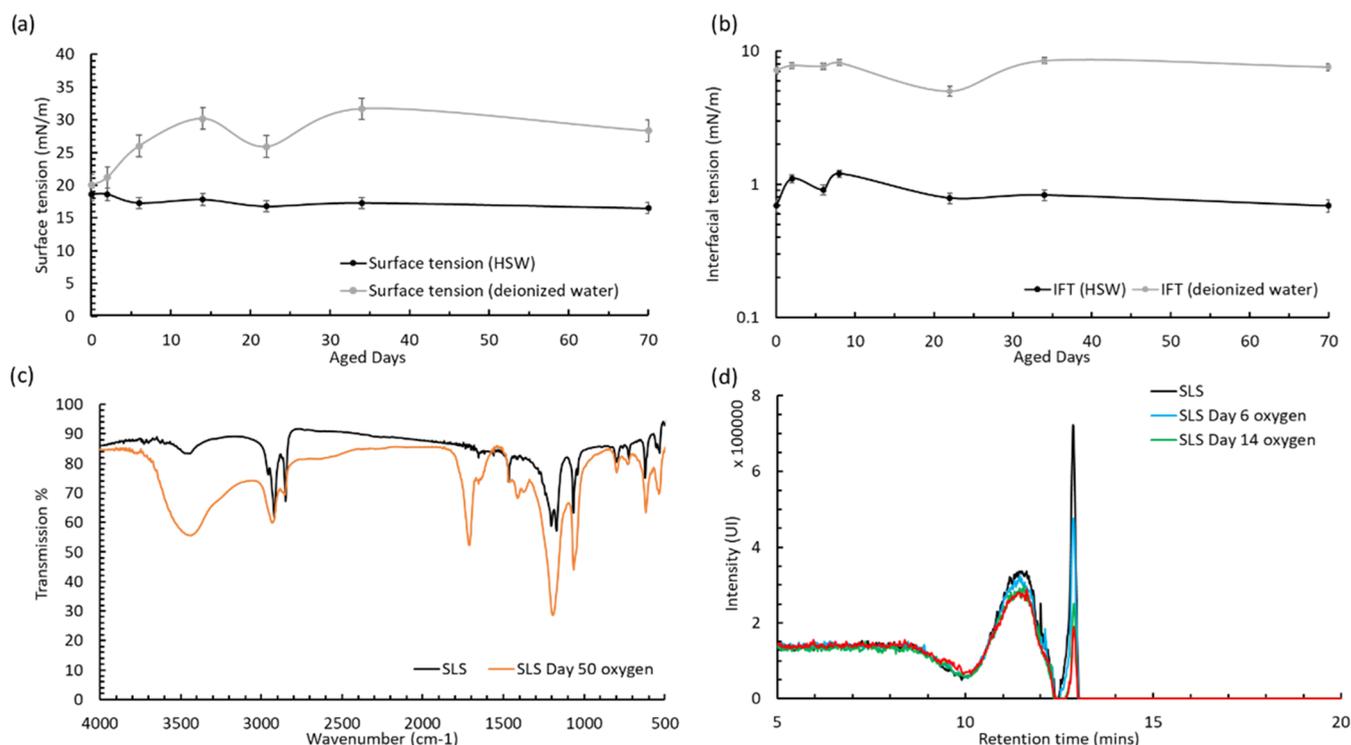


Figure 8. (a) Surface tension of SLS in HSW and deionized water under thermal aging at 95 °C in 70 days when dissolved oxygen was not removed; (b) interfacial tension of SLS in HSW and deionized water for 70 days when dissolved oxygen was not removed; (c) IR spectra of SLS aged for 50 days; and (d) HPLC spectra of SLS before and after aging in a month. The error bars present three measurements.

(equation shown in Figure 7) arises from the cleavage of C–N and Hofmann elimination. It proceeds via a nucleophilic attack of the anion on the β -hydrogen, relative to the nitrogen atom. The long chain is eliminated from the nitrogen, resulting in an alkene, a tertiary amine, and a protonated anion.^{36,37} The very small difference observed in Figure 6d, characterized by a spike around 1150 cm⁻¹ that disappeared, may indicate weakening of the C–N vibration in the headgroup. Considering the stability of SB3–14 in the IR spectra, the degradation of the sulfobetaine surfactant could possibly be similar to the quaternary

ammonium with elimination from quaternary nitrogen and formation of the corresponding alkene, instead of hydrolysis of sulfonate.

In summary, the IR results indicate that the instability of carboxylate is due to the transformation into the corresponding acid and precipitation from the solutions. The sulfonate and sulfate decompositions are due to the hydrolysis of the anionic head, forming alcohol and NaHSO₃/NaHSO₄. The possible decompositions of sulfobetaine and quaternary ammonium are mostly caused by elimination of the ionic head, forming the

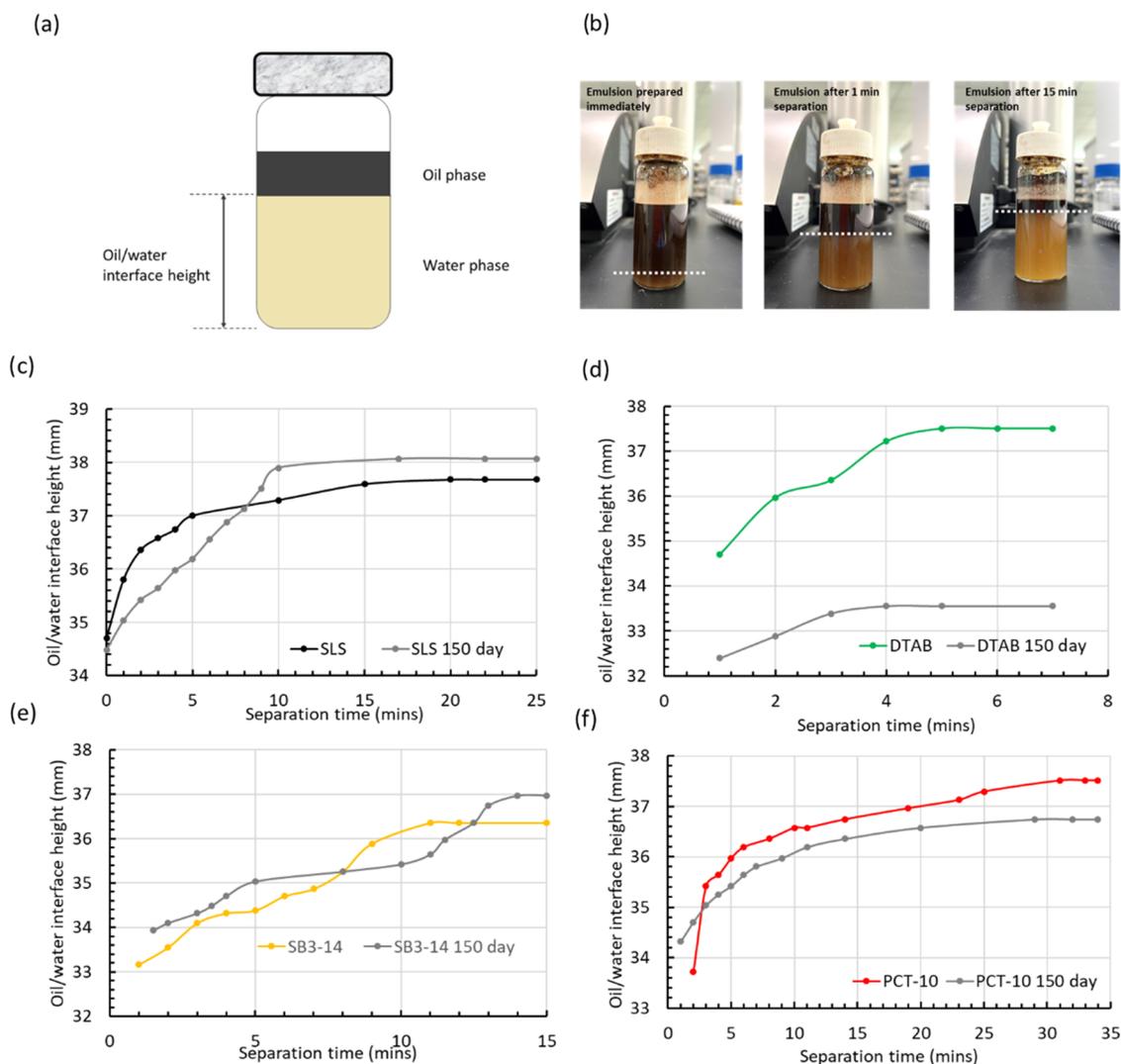


Figure 9. (a) Scheme of oil/water interface height in the test, (b) water/oil separation versus time in SB3–14, and oil/water interface height versus time in (c) SLS, (d) DTAB, (e) SB3–14, and (f) PCT-10.

corresponding alkene and amine. It is reasonable that the decomposition of sulfobetaine and quaternary ammonium requires a higher activation energy, and these two surfactants are more stable than sulfonate and sulfate surfactants.

3.5. Effects of Oxygen on Long-Term Thermal Stability. Although the oil reservoir itself is mainly an anaerobic environment, the oxygen could dissolve in the solution during the preparation process on the ground. Thus, risks of surfactant degradation still exist. The degradation of SLS was investigated when the oxygen in the solution was not removed.

Figure 8a,b shows the surface tension and IFT of 0.2% in HSW and DI water without oxygen removal, aged for 70 days, respectively. It turned out that the surface tension of SLS in HSW slightly decreased from 18.6 to 16.5 mN/m, while the value of that in DI water increased from 20.0 to 28.3 mN/m. The IFT change is less sensitive than surface tension. The IR spectrum in Figure 8c clearly shows that the two sharp peaks of the $-S=O$ stretching vibration transformed into one strong peak after 50 days of aging because of the hydrolysis of the sulfonate group. Besides, the peak intensity in the HPLC spectra of SLS in HSW under aging for 6, 14, and 34 days in Figure 8d decreased with aging time. The SLS peaks of longer-aged samples were quite weak and could no longer be clearly

identified. This experiment demonstrates that the presence of oxygen in the preparation stage will significantly speed up the hydrolysis of sulfonate groups.³⁸ This should be considered during application.

3.6. Emulsifying Ability. Previous studies and pilot applications have shown that the oil production rate can be obviously improved with the formation of emulsions in surfactant-mediated injection techniques. The good emulsification of oil in surfactant solutions could yield favorable interfacial properties and mobilize the trapped oil in porous media.³⁹ Therefore, it is meaningful to compare the emulsifying ability of nonaged and 150-day-aged surfactant samples in HSW of the different types. After emulsion solutions were prepared, the height of the oil/water interface to the bottom of the sample bottle was determined. The absolute height value is based on the volume of the water phase and the oil phase. In a specific 20 mL system, the 18 mL water phase height is about 38 mm and the total height is 42 mm. The height versus separation time, indicating the water/oil phase separation rate, was used to represent the emulsion stability in surfactant solutions (Figure 9a). A longer time to reach a plateau indicates the better emulsifying ability of the surfactant. In Figure 9b, we also present the photos of emulsion solutions in SB3–14 that were prepared

by high-speed stirring immediately, after 1 min separation, and after 15 min separation, respectively. Figure 9c–f presents the oil/water interface height versus time in SLS, DTAB, SB3–14, and PCT-10 solutions in HSW at 95 °C, respectively. The results showed that the emulsifying ability of the four surfactants was similar before and after thermal aging, consistent with the interfacial tension and HPLC results in HSW. The separation time of SLS before and after thermal aging was both about 10 min. The values were 5 and 4 min in the cases of nonaged and 150-day-aged DTAB, respectively. For the aged SB3–14 solutions, the separation time was 13 min, slightly longer than that of 11 min before aging. (Two minutes can be regarded as system error.) As for PCT-10, the curves of interface height versus time followed an identical trend with separation times, which were both longer than 25 min. All of the surfactants presented a similar emulsifying ability before and after thermal aging. However, it presented a much weaker emulsion stability in quaternary ammonium than in the other two types of surfactants. Combined with the previous thermal stability sequence, sulfobetaine could be a better option for surfactant-mediated chemical injection in high-salinity high-temperature reservoirs.^{40,41}

4. CONCLUSIONS

To provide insights into surfactant selection for chemical injection to improve oil production, this work systematically investigated the long-term thermal stability of six surfactants (LAS, SLS, SDS, DTAB, SB3–14, and PCT-10), representing five types of surfactants (carboxylate, sulfonate, sulfate, quaternary ammonium, and sulfobetaine) aged at 95 °C for 150 days, and elucidated the degradation mechanism. The following can be concluded from the results.

- (1) The overall long-term stability sequence of surfactant solutions is sulfobetaine \approx quaternary ammonium > sulfonate > sulfate > carboxylate. SB3–14, PCT-10, DTAB, and SLS were slightly decomposed (\sim 10%) in HSW, with surface tension and interfacial tension not being affected, while LAS precipitated and more than 90% of the SDS decomposed.
- (2) The sulfonate and sulfate decompositions are due to the hydrolysis of the anionic head, forming the alcohol and NaHSO₃/NaHSO₄. This helps explain the stability of the surfactants, while the slight degradations of sulfobetaine and quaternary ammonium are possibly caused by elimination of the ionic head, forming the corresponding alkene and amine. The carboxylate is possibly transformed into the corresponding acid form and precipitates from the solution although it has the highest temperature tolerance in the solid state.
- (3) The presence of oxygen in sulfonate solutions will significantly speed up the hydrolysis of sulfonate groups. This should be taken into consideration in the surfactant preparation stage during applications.
- (4) The sulfobetaine surfactant presented a superior ability to stabilize oil/water emulsions before and after thermal aging. Thus, it is recommended for long-term surfactant injection operations for high-salinity high-temperature reservoirs.

This work has suggested that sulfobetaine surfactants are the most promising and cost-effective for injection in a high-temperature high-salinity field, which are worth developing in subsequent studies. The second choice could be cationic

surfactants or sulfonate surfactants, while the carboxylate surfactant should be improved by introducing hydrophilic groups into the molecules.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.3c09734>.

Surface tension measured by the plate method and the spinning drop method; surface tension and IFT in water and HSW at 95 °C, respectively; thermogravimetric analysis result of the selected surfactants; and pH value of the surfactant solutions in HSW (PDF)

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Notes

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■ ABBREVIATIONS

LAS	dodecyl carboxylic sodium
SDS	sodium dodecyl sulfate
SLS	sodium dodecyl sulfonate
DTAB	dodecyltrimethylammonium bromide
SB3–14	3-(<i>N,N</i> -dimethylmyristylammonio) propanesulfonate
HSW	high-salinity water

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