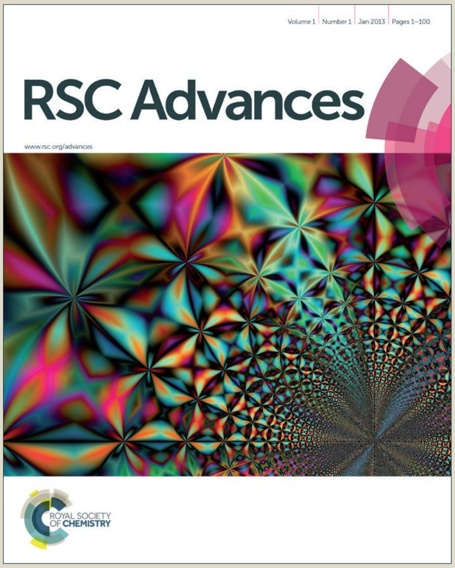
RSC Advances

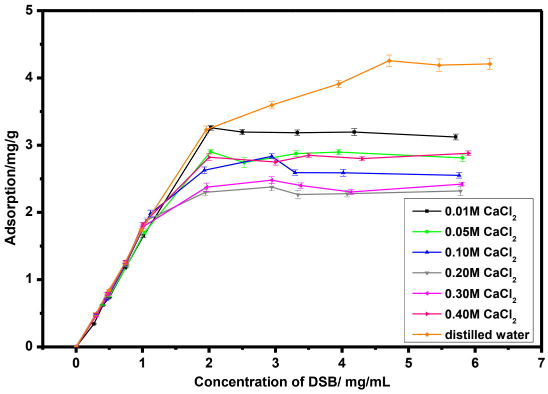


ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Adsorption behavior of dodecyl hydroxypropyl sulfobetaine on limestone in high salinity water

Yang Wang, Jijiang Ge*[1], Guicai Zhang, Ping Jiang, Wen Zhang, Yang Lin
China University of Petroleum (East China) Qingdao China 266580



Highlights: With increase of $CaCl_2$ concentration, equilibrium adsorption of DSB on limestone decreases first and then increases.

Abstract: Herein is presented a new methodology to determine the static adsorption of dodecyl hydroxypropyl sulfobetaine (DSB) on limestone with the use of HPLC. The results showed that with the increase of NaCl concentration, adsorption of DSB on limestone surface decreased due to increase of zeta potential (less negative). In contrast, with increasing $CaCl_2$ concentration, adsorption of DSB decreased first and then increased, which corresponds to the change trend of limestone surface zeta potential. As to the influence of temperature, with increase of temperature, adsorption of DSB increased slightly. The behavior of DSB adsorption under different temperatures could be well interpreted by more adsorption of Ca^{2+} at higher temperature. It was also found that a little addition of inorganic salt could accelerate formation of vesicles and more salt would inhibit the formation. By comparison of aggregation distribution before and after adsorption, it was found that micelles contribute more to adsorption than vesicles.

1. Introduction

Betaine surfactants have recently attracted increasing attention for their advantages such as good tolerance to high temperature and high salinity, high hardness, and high interfacial activity at low concentration [1-2].

With oilfield development, more and more oilfields [3-5] with high temperature and high salinity are needed to develop.

Based on that, betaine is a promising surfactant, especially to high salinity and high

---

[1] Jijiang Ge (1972-), professor of China University of Petroleum (East China), E-mail:wyang2235@126.com, address: Qingdao economic & technology development zone, Qingdao, China.

temperature reservoirs. In addition to inherent tolerance to high salinity, betaine could improve other surfactants' tolerance to divalent ions. Xu et al. [6] found that the addition of DSB can improve the tolerance to Ca^{2+} and Mg^{2+} of alkyl carboxylates. Negative groups are formed at the surface of the micelle, enabling Ca^{2+} and Mg^{2+} to be complexed, and improving the tolerance to Ca^{2+} and Mg^{2+} of the alkyl carboxylate. Besides, betaine is a good foaming agent and foam booster. Zhao et al. [7] achieved a good foaming formulation with DSB as the main foaming agent. With the addition of dodecanol and quaternary ammonium salt, this system had good foaming properties. Li et al [8] found that at low salinity, many surfactants such as Triton X-200, sodium 16-18 alpha olefin sulfonate(AOS16-18), sodium 15-18 internal olefin sulfonate (IOS15-18) were good foaming agents. However, without adding betaine at the optimal ratio, none of the surfactants or their blends would generate strong foams in the presence of residual crude oil. In Li's work, it should be noted that the mixture of IOS15-18 and betaine did not work in either water-wet or oil-wet carbonate sandpack due to possible surfactant adsorption. So in the application of surfactant, adsorption is an inevitable problem.

In carbonate reservoirs, the surface chemistry of carbonates in aqueous solutions has an important influence on surfactant adsorption. The conduct of adsorption between the surface of the adsorbent and the adsorbed species is usually considered to be led mainly by the following aspects (1) electrostatic interactions (2) chemical interactions (3) hydrophobic lateral interactions (4) hydrogen bonding (5) desolvation energy, while not every system contains all the five aspects [9-12]. With the change of the adsorbent and the adsorbed species as well as the environment, the above interactions are varied.

In enhanced oil recovery (EOR) applications, among all the mentioned aspects, electrostatic interaction is always very important. So the surface charge of solid surface plays a prominent role. Tahe oil field is a vuggy-fractured limestone reservoir in western China. The most important feature and most difficulty in exploration is its high salinity. Most formation water of Tahe oilfield is above 200,000mg/L. In such harsh aqueous media, a solid surface may have a different surface charge from one in low salinity. Besides, traditional surfactants cannot behave well for EOR performance, while a betaine could perform better because of good tolerance to high salinity. In field application of surfactant EOR, surfactant adsorption is a key factor. High adsorption will cause much surfactant consumption. In this work, a methodology was established for measuring the adsorption of DSB at different temperatures and in the presence of different salt stress. Aggregation of surfactant under different salt stress was studied and the relationship between adsorption and aggregation is preliminarily discussed. This report is a detailed study of adsorption in different aqueous medium and zeta potential.

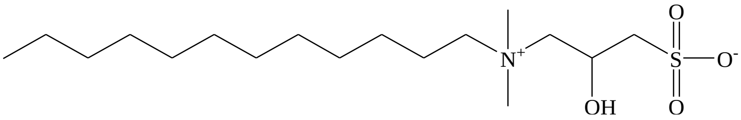
2. Experimental section

2.1. Equipment.

High-performance liquid chromatography (HPLC) measurements were performed in an Agilent 1100 chromatograph using a Nova-Pak HR C18 column. Dynamic light scattering measurements are performed with a spectrometer and a Spectra-physics 2017 200mw Ar laser. The scattering angle is 90 °, and the intensity autocorrelation functions are analyzed by using the Contin and Cumulant methods.

2.2. Materials.

Surfactant: DSB was prepared in laboratory and specific synthetic method was stated in the work of Wang et al [13]. The molecular formula of DSB is as following.



The sulfobetaine surfactant was purified as follows: the isopropanol solvent in the reaction product was first removed with a rotary evaporator, and then the reaction product was recrystallized 2-3 times from ethanol at 0℃ Finally, a white crystal crystalline powder was obtained after vacuum desiccation at 60℃.

Methanol and water were purchased from J.T.Baker (at HPLC grade). The composition of Tahe formation water is shown in Table 1.

Table 1 Ion composition of Tahe formation water

ion content/($mg\cdot L^{-1}$)							total salinity /($mg\cdot L^{-1}$)	pH	water type
Cl^-	HCO_3^-	CO_3^{2-}	Ca^{2+}	Mg^{2+}	SO_4^{2-}	Na^++K^+			
137529.5	183.6	0	11272.5	1518.8	0	73298.4	223802.8	5.8	$CaCl_2$

2.3. Rock Treatment.

Tahe limestone was used as a mineral substrate. The rock was passed through a mesh sieve number 80, to obtain particles with a mean surface area of 3.0 m^2/g. The rock was then washed with sequential refluxes in a Soxhlet system using hexane, toluene, chloroform, and methanol, then dried at 40 ℃ in an oven, and finally allowed to dry at room temperature for 72 h. XRD analysis results of limestone are shown in Table 2.

Table 2 XRD analysis results of limestone.

Mineral content					
Quartz	Potash feldspar	Calcite	Siderite	Pyrite	Clay mineral
17	2	71	1	1	8

2.4 Measurement of zeta potential

Phase-analysis light-scattering technique was applied to determine the zeta potential of limestone particles. The solution of solid/brine sample was prepared by adding 1wt% of solid powder to the brine, and then the powder suspension was established by dispersing it for two minutes with ultrasonic oscillator. The pH of the solution was adjusted by using either HCl or NaOH solution, and the measurements were conducted at pH = 5.8 unless stated otherwise.

2.5 Static Adsorption of the Surfactant.

Adsorption isotherms were determined by batch equilibrium adsorption procedures. Samples of 5.00 g of limestone previously treated were placed in 100mL beakers. To each sample, 15 mL of surfactant dilutions were added. Surfactant solutions were prepared at different concentrations with different NaCl or $CaCl_2$ concentrations. The samples were stirred for 12h at ambient temperature and then left to repose for 2 h. Each sample was passed through HPLC filters. The solutions were analyzed by HPLC to determine the surfactant concentration according to eq1.

$$A=\frac{(\rho_{o}-\rho_{x})V}{\mathrm{m}} \tag{1}$$

Where "A" is milligrams of surfactant per gram of limestone(mg/g), "ρ_0" is the initial surfactant concentration, "ρ_x" is the concentration of the surfactant after the adsorption, "V" is the volume of the surfactant solution added to the sample (mL), and "m" is the mass of limestone (g).

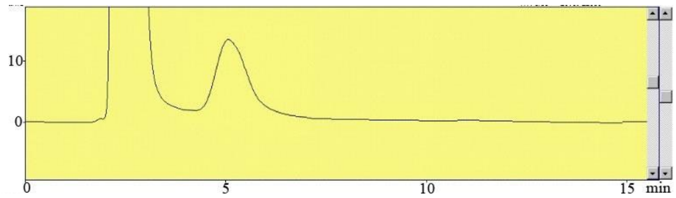
3 Results and discussion

3.1 HPLC method to measure betaine surfactant concentration

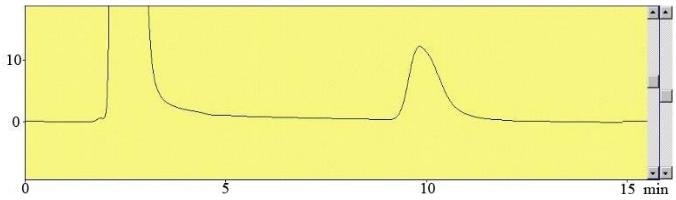
Different from betaines with amide groups ($-CONH_x$), DSB has no UV adsorption. As a consequence, the concentration of DSB in solution was measured on a Shimadzu LC-10 liquid chromatograph with refractive index detection (RID-10A), which is similar to the method of Li et al [14].

3.1.1 Determination of methanol to water ratio

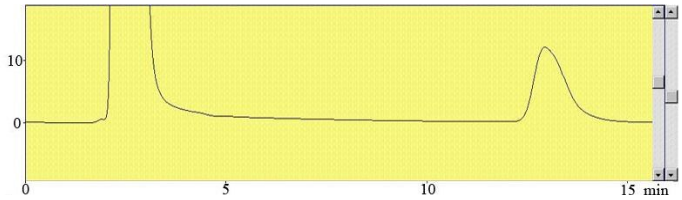
Compared with sulfobetaine surfactant in Li t al's work [14], DSB has shorter carbon chain and a shorter retention time. Therefore, a mobile phase of higher methanol-to-water ratio was adopted. When the ratio of methanol to water was 80:20, 75:25 and 70:30, respectively, HPLC results are shown in Figure 1. From the results, considering retention time, the ratio of methanol and water in the mobile phase is chosen as 75:25.



Methanol: water=80:20



Methanol: water=75:25



Methanol: water=70:30

Figure 1 HPLC results of DSB at various methanol/water ratio

3.1.2 Effect of inorganic salt

After the adsorption test, surfactant solution was analyzed by HPLC after centrifugation. In order to study the effect of inorganic salt on retention time and peak area, 3mg/mL DSB solution in 0.1M$CaCl_2$, 1M NaCl and distilled water were prepared and HPLC tests were conducted. All the tests were repeated 3 times. Retention times and peak areas are shown in table 3. From the results, it can be found that, among all the three solutions, retention time varied, but they all had similar peak area at the same surfactant concentration. These results validate the use of HPLC, under these conditions, to determine DSB concentrations.

Table 3 Peak area and retention time in different tests.

Inorganic salt	Peak area	Retention time/min
0.1M $CaCl_2$	4797832	9.96
0.1M $CaCl_2$	4800318	9.95
0.1M $CaCl_2$	4789931	9.95
1M NaCl	4809814	8.48
1M NaCl	4802419	8.46
1M NaCl	4798667	8.50

3.1.3 Column Temperature and Flow Velocity.

The tests indicate that, with the decrease of the flow velocity of the mobile phase, the retention time becomes longer and the peak shape becomes wider and shorter and with the increase of the column temperature, the retention time becomes a little shorter. According to these results, the velocity of the mobile phase is set as 0.75mL/min and the column temperature is fixed at 40℃.

Shown in Figure 2 is the standard calibration curve for DSB based on the HPLC method.

It indicates that the chromatographic integral area exhibits a good linear relationship with the concentration of DSB in the range of 0.1-7 mg/mL.

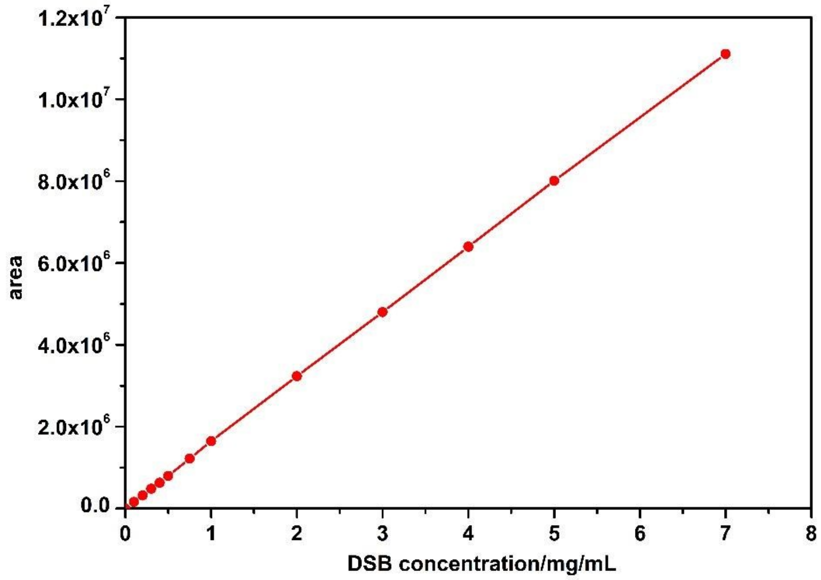


Figure 2 Standard calibration curve of measuring DSB concentration

3.2 Effect of inorganic salt on adsorption

In Tahe formation water, NaCl and $CaCl_2$ are the main inorganic salts. Ca^{2+} is the potential determining ion. Compared with Ca^{2+}, Na^+ cannot determine the electrical potential, but it can compress the diffuse electric double layer, so the zeta potential value can be affected. In our study, the effect of NaCl and $CaCl_2$ on zeta potential and adsorption were studied.

3.2.1 Effect of NaCl on zeta potential and adsorption

The adsorption of DSB on the surface of limestone in solutions with different concentrations of NaCl was measured at 25℃. NaCl concentrations varied from 0.1M to 3M. The results are shown in Figure 3. It could be found that, with the increase of NaCl concentration, equilibrium adsorption of DSB on limestone decreased. Our findings were opposite to the results of Nieto-Alvarez et al[15].

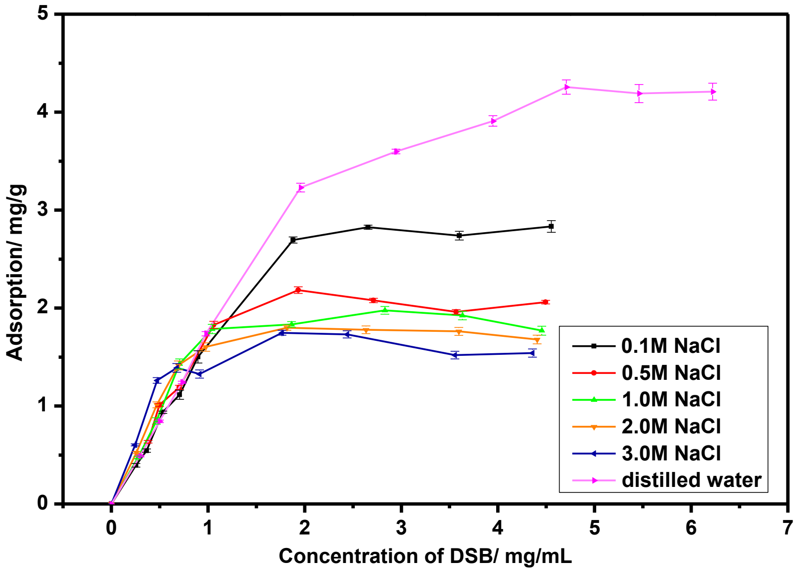


Figure 3. Adsorption of DSB on limestone in NaCl solutions at 25 ℃

In the study of Nieto-Alvarez et al [15], with the increase of water salinity, equilibrium adsorption increased. Cocamidoproyl hydroxysultaine (in the study of Nieto-Alvarez et al) has a similar structure and property to DSB used in our study. Differences between surfactants would not invert the adsorption behavior observed in the current work. In our opinion, the main difference between the two studies is the rock. Though both rocks are limestone, differences in composition may result in different zeta potentials. As is well known, electrostatic interactions play a governing role in the adsorption process [16].

In general, carbonate exhibited a positively charged surface. However, in our previous study [17], it was found that, with the increase of quartz content, zeta potential decreased to negative. Vdović and Bišćan [18] also found that natural calcite was more negatively charged than the synthetic calcite. It was thought that a very small amount of impurities possibly led to significant changes of zeta potential [10]. With the increase of NaCl concentration, adsorption of DSB on Tahe limestone decreased dramatically then changed smoothly. Addition of NaCl compresses the diffused double layer, so electrostatic interaction between DSB and limestone will become weaker and equilibrium adsorption will be smaller. It should be noted that the decrease in adsorption is not proportional to NaCl concentration. In order to investigate the factors affecting equilibrium adsorption, zeta potentials of Tahe limestone in different concentrations of NaCl solution were measured. The results are shown in Figure 4. It was found that with the increase of NaCl concentration, the change in zeta potential has a similar trend as equilibrium adsorption. However, even as the NaCl concentration reached 3mol/L, zeta potential is still negative. Figure 5 shows the change of adsorption versus zeta potential.

It was found that, with the increase of zeta potential (less negative), equilibrium adsorption decreased approximately linearly. The results confirm that electrostatic interaction is a governing role in the adsorption process. In the study of Li et al [14], with increasing NaCl concentration, the adsorption of sulfobetaine decreased first and then increased. In our study, no increase of adsorption was observed. As to the reason, with the increase of NaCl concentration, solubility of sulfobetaine with carbon chain length of 17 decreased. DSB has a shorter carbon chain, so it possesses a better solubility even at high NaCl concentration.

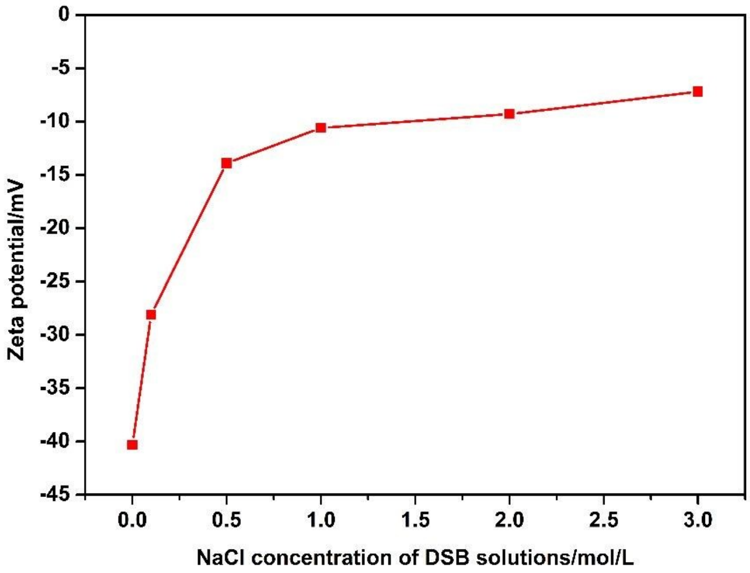


Figure 4 Zeta potential of limestone in NaCl solutions at 25 ℃

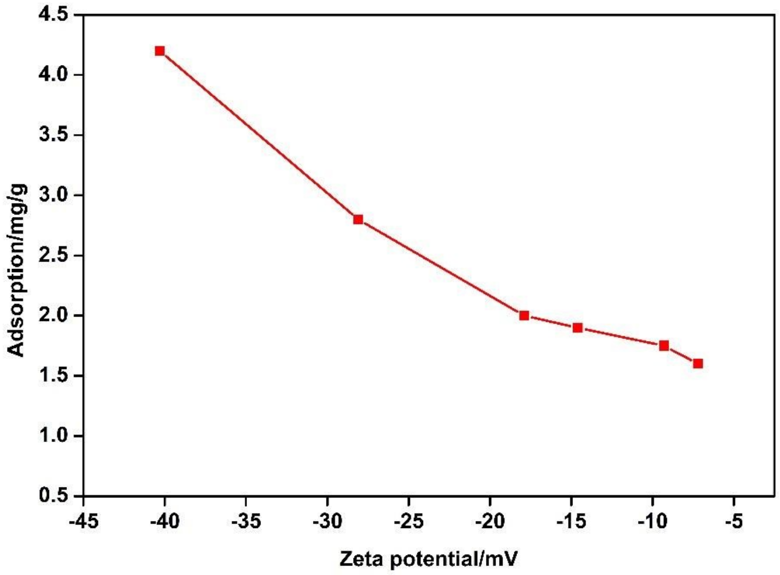


Figure 5 Adsorption change with zeta potential in NaCl solutions at 25 ℃

3.2.2. Effect of $CaCl_2$ on zeta potential and adsorption

As well as NaCl, another main inorganic salt in Tahe formation water is $CaCl_2$. With limestone, Ca^{2+} is the potential determining ion [21-22], which has an important impact on the surface charge (zeta potential). Previous study indicates that addition of NaCl cannot alter surface charge from negative to positive. As to $CaCl_2$, the effect of $CaCl_2$ concentration on adsorption was studied, and the results are shown in Figure 6.

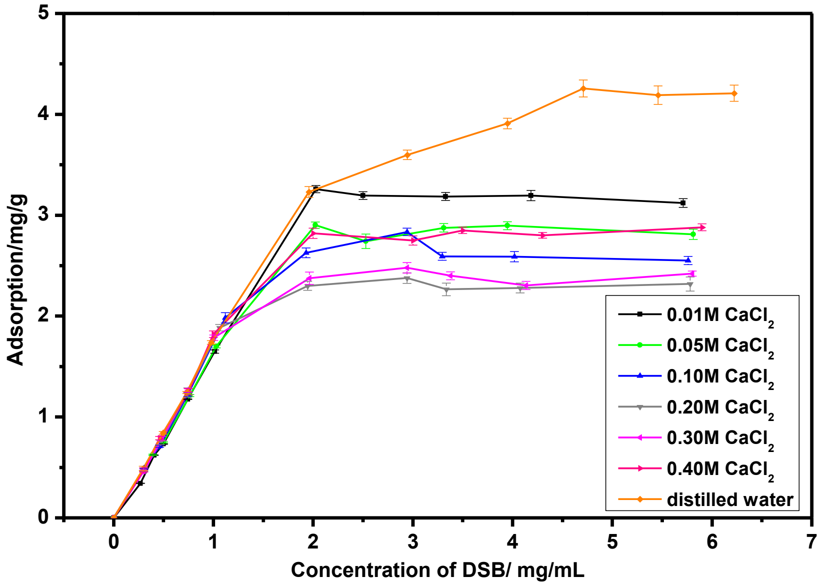


Figure 6 Adsorption of DSB on limestone in $CaCl_2$ solutions at 25 ℃

In general, with the increase of $CaCl_2$ concentration, adsorption of DSB in $CaCl_2$ solutions on limestone decreased as in NaCl solution. However, it should be noted that, compared with adsorption in 0.3M $CaCl_2$, when the $CaCl_2$ concentration was 0.2M, adsorption was lower. Hu et al [19] studied the adsorption behavior of DSB on a silica/solution interface with $Ca^{2+}$and Mg^{2+} existing in aqueous solution by atomistic molecular simulations.

The results showed that the adsorption of the betaine surfactant had three possible configurations. First, when there is no Ca^{2+} in the aqueous solution, the DSB molecule oriented to the solid surface with the quaternary nitrogen group approaching the surface and the anionic group moving away. Strong negative interaction energies in this system cause the adsorption to occur easily. With the existence of Ca^{2+} in aqueous solution, an oblique adsorption of the DSB molecule can occur. In this way, the anionic part of DSB is closer to the silica surface as the result of attraction between Ca^{2+} and the sulfonate group of DSB, while the cationic, quaternary ammonium part of DSB was attracted by the net negative charge of surface. With further increase of Ca^{2+}, a vertical configuration emerged. From simulation results of Hu et al, it could be found that, among all three adsorption types, DSB has largest cross-sectional molecular area in the second mode.

Meaning, DSB has minimum value of adsorption. As to our result, with the increase of Ca^{2+}, adsorption of DSB decreased first because of the emergence of the second adsorption type. With further increase of Ca^{2+}, the third adsorption configuration can occur, so adsorption increased. When the $CaCl_2$ concentration was above 0.2M and with the increase of $CaCl_2$ concentration, adsorption of DSB on limestone increased. The results could also be interpreted via zeta potential. Zeta potential values of limestone in $CaCl_2$ solution are shown in Figure 7. From Figure 7, it could be found that the zeta potential of limestone increased with the increase of $CaCl_2$ concentration in aqueous solution, which was similar to the change in NaCl solution. However, the biggest difference was that, with the increase of $CaCl_2$ concentration, zeta potential of limestone became positive, while in NaCl solution, even when the NaCl concentration was 3M, zeta potential of limestone was still negative. When there was no Ca^{2+} in solution, DSB adsorb on the solid surface by the first adsorption configuration. When $CaCl_2$ concentration was under 0.2M, zeta potential was still negative. In this case, some molecules adsorb on solid surface by the first adsorption configuration and some molecules by the second manner. It means that both of the first and the second adsorption configuration co-exist. In this range, with increase of $CaCl_2$ concentration, the ratio of molecules by the first and second adsorption manners decreases and adsorption decreases. When $CaCl_2$ concentration was about 0.2M, zeta potential was about 0 and DSB has minimum adsorption value in $CaCl_2$ solutions. As to the reason, in this case, most DSB molecules adsorb on solid surface by the second configuration and the attraction between anionic groups and Ca^{2+} is strong, while the cationic, quaternary ammonium part of DSB has little interaction with surface due to the small value of zeta potential. With further increase of $CaCl_2$ concentration, zeta potential became positive, so the repulsion between cationic groups and Ca^{2+} and the attraction between anionic groups and Ca^{2+} would make DSB molecule adsorb on the surface in a vertical way, which corresponds to the third adsorption configuration. By the third adsorption configuration, DSB molecule has smaller cross-sectional area, so adsorption increases.

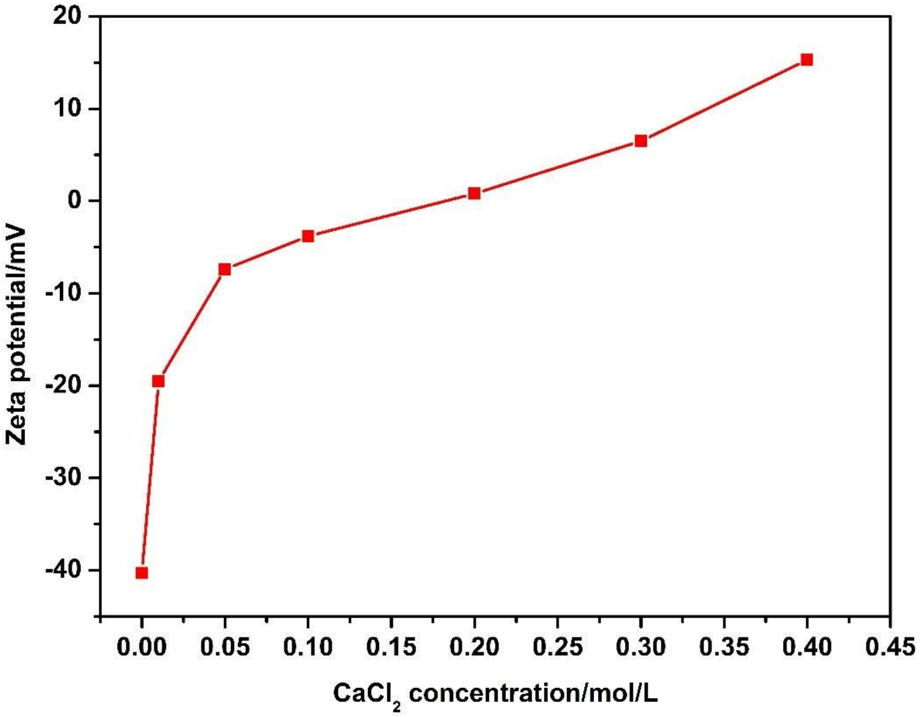


Figure 7 Zeta potential of limestone in $CaCl_2$ solutions at 25 ℃

3.3 Effect of temperature on adsorption

Temperature has an effect on the wettability of limestone due to adsorption of surfactant or ions, so it plays an important role in EOR. Because of the importance of temperature in EOR, the influence of such a parameter was evaluated in the process of adsorption of DSB at various concentrations on limestone in Tahe formation water at 25 ℃, 50 ℃ and 80 ℃, respectively. The results of adsorption are shown in Figure 8. From Figure 8, it could be found that, with increasing temperature, adsorption of DSB on limestone increased slightly. Because of the exothermic nature of most of the interactions of this type [15], the adsorption decreases as the temperature is increased. So our results looks a paradox. From the simulation results of Hu et al [20], it was demonstrated that DSB adsorbed on limestone surface via Ca^{2+}. It meant that the adsorption configuration is different from adsorption without Ca^{2+}. Therefore, the adsorption of Ca^{2+} on limestone will influence the adsorption of DSB. In addition, adsorption of Ca^{2+} on limestone will influence the zeta potential, so zeta potential of limestone in formation water at different temperatures was measured and the results are shown in Table 4. From Table 4，it could be found that, with the increase of temperature, the zeta potential of limestone increased (more positive). It meant that, at higher temperature, more Ca^{2+} adsorbed on the limestone surface. This evidence could be used to explain the trend that the adsorption of DSB on limestone increased with the increase of temperature.

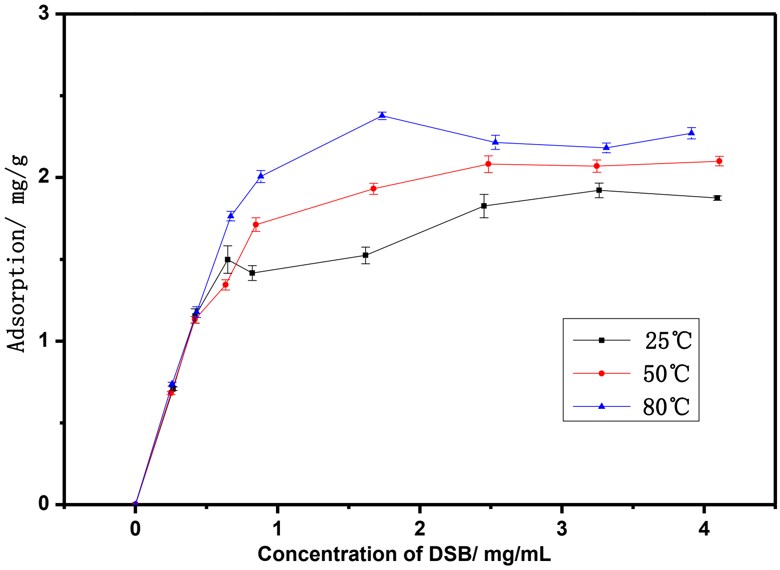


Figure 8 Adsorption of DSB on limestone at different temperatures in Tahe formation water

Table 4 Zeta potential of limestone in Tahe formation water at different temperatures

Temperature/℃	Zeta potential/mV
25	3.2
50	15.1
80	27.7

3.4 Effect of DSB aggregation on adsorption

Surfactants in aqueous solution can have various aggregation forms. The presence of high salinity in an aqueous solution has been reported to promote the transition from micelle to vesicles. Vesicles usually have larger volumes and present lower adsorption toward the solid surface because of steric hindrance. In view of the effect of particle size on adsorption, aggregation sizes of DSB in different solutions were measured. Just like adsorption measurement, aggregation size of DSB was measured in NaCl and $CaCl_2$ solutions of different concentrations. The results are shown in Figure 9 and Figure 10, respectively. In these measurements, DSB concentration were held constant at 1mg/mL.

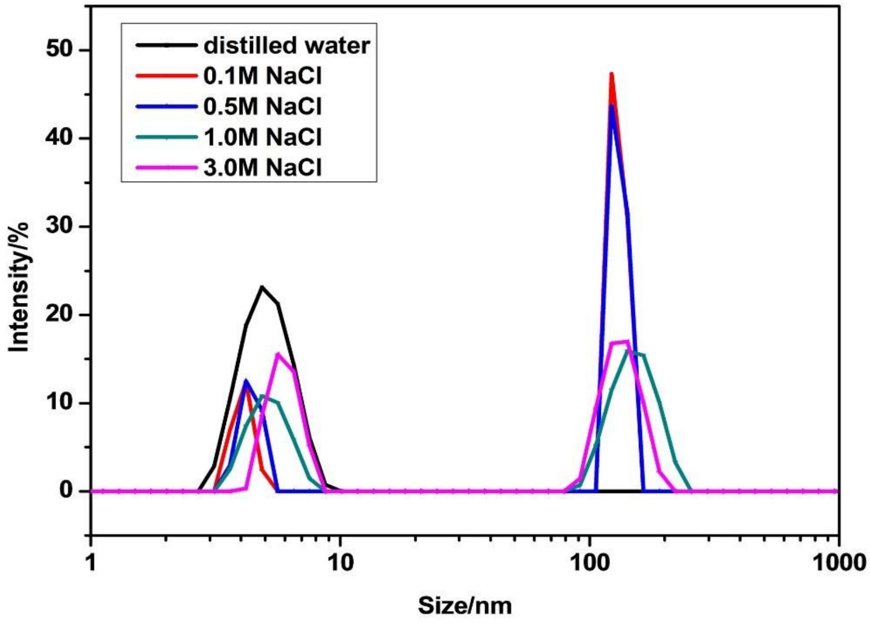


Figure 9 Aggregation size of DSB in different NaCl solutions

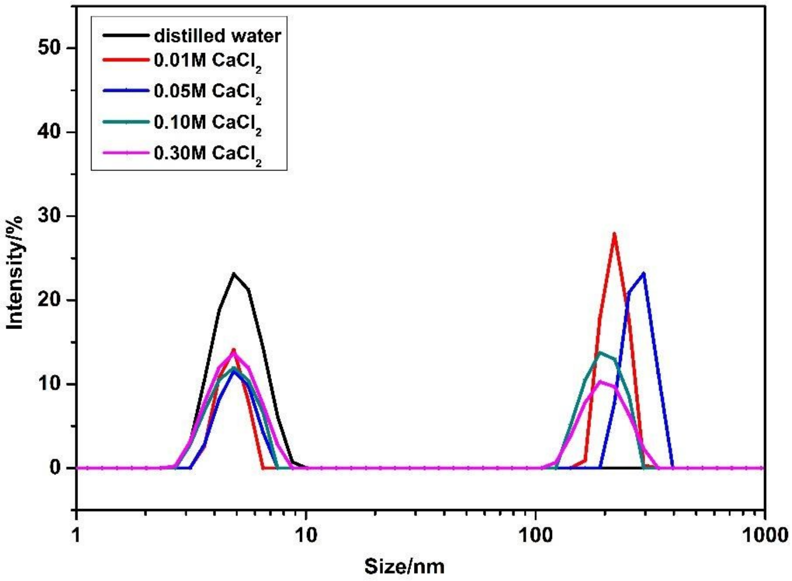


Figure 10 Aggregation size of DSB in different $CaCl_2$ solutions

From Figure 9 and Figure 10, it could be found that the influence of NaCl and $CaCl_2$ on DSB aggregation size was similar. First, with the addition of inorganic salt, the intensity of DSB aggregation around 100nm increased obviously. With further increase of inorganic salt concentration, the intensity of DSB aggregation around 10nmincreased. It meant that a small amount of inorganic salt could favor the formation of vesicles, while further addition of inorganic salt would inhibit the formation. In Nieto-Alvarez et al's study [15], the results showed that formation of vesicles was responsible for the decrease of adsorption at high surfactant concentrations. Different from Nieto-Alvarez et al's study, the formation of vesicles occurred at low inorganic salt, so no adsorption decrease was detected in our study. The aggregation size of DSB solution before and after adsorption was studied and the results are shown in Figure 11. In this study, the DSB concentration was 2mg/mL and Tahe formation water was the aqueous medium. From Figure 11, it could be found that, compared with intensity before adsorption, intensity of aggregation around 10nm decreased substantially. This means that between aggregation of 10nm (micelle) and 100nm (vesicle), micelles were the main contribution to adsorption. As stated before, because of steric hindrance, vesicles exhibit low adsorption on a solid surface.

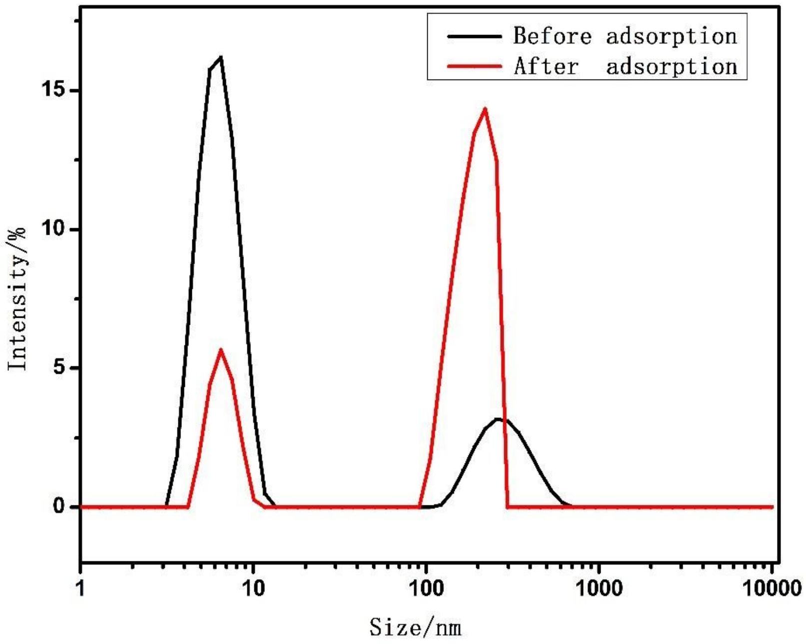


Figure 11 Intensity of DSB aggregation before and after adsorption

4 Conclusions

(1) An HPLC method was established to measure DSB concentration.

(2) With the increase of NaCl concentration, adsorption of DSB on limestone surface decreases due to decrease of zeta potential.

(3) In $CaCl_2$ solution, with the increase of $CaCl_2$ concentration, zeta potential of limestone surface increases and when the $CaCl_2$ concentration is above 0.2M, the zeta potential becomes positive. A minimum value of DSB adsorption appeared with changing zeta potential.

(4) With the increase of temperature, adsorption of DSB increased slightly.

(5) Micelles contribute more to adsorption than vesicles.

Acknowledgements

Financial support by the National Natural Science Foundation of China (51104170) and the Natural Science Foundation of Shandong Province (No.ZR2014EZ002, ZR2012EEM007) and the Fundamental Research Funds for the Central Universities (14CX06088A) and “Innovation project of China University of Petroleum” (YCX2015012) are gratefully acknowledged.

References

[1] Wang, D., Liu, C., Wu, W., & Wang, G.. Development of an ultralow interfacial tension surfactant in systems with no-Alkali for chemical flooding. SPE Symposium on Improved Oil Recovery. Society of Petroleum Engineers, 2008.

[2] Wang, D., Liu, C., Wu, W., & Wang, G. Novel Surfactants that Attain Ultra-Low Interfacial Tension between Oil and High Salinity Formation Water without adding Alkali Salts Co-surfactants Alcohols and Solvents. SPE EOR Conference at Oil & Gas West Asia. Society of Petroleum Engineers, 2010.

[3] Puerto, M., Hirasaki, G. J., Miller, C. A., & Barnes, J. R. Surfactant systems for EOR in high-temperature, high-salinity environments[J]. SPE J, 2012, 17(1): 11-19.

[4] Shupe R D, Maddox Jr J. Surfactant oil recovery process usable in high temperature, high salinity formations: U.S. Patent 4,077,471[P]. 1978-3-7.

[5] Levitt, D. B., Dufour, S., Pope, G. A., Morel, D., & Gauer, P. Design of an ASP flood in a high-temperature, high-salinity, low-permeability carbonate[C]//Paper IPTC 14915, presented at the International Petroleum Technology Conference, Bangkok, Thailand. 2012: 7-9.

[6] Xu, J., Sun, W., Li, G., Xu, J., Zheng, L., Wang, H., & Zhang, G. Investigation in extremely improved ability of resisting Ca^{2+} and Mg^{2+} for alkyl carboxylates flooding system with adding DSB. Chemical Journal of Chinese Universities. 2007, 28(3):496-501.

[7] Zhao, L., Li, A., Chen, K., Tang, J., & Fu, S.. Development and evaluation of foaming agents for high salinity tolerance[J]. Journal of Petroleum Science and Engineering, 2012, 81: 18-23.

[8] Li, R. F., Hirasaki, G., Miller, C. A., & Masalmeh, S. K.. Wettability Alteration and Foam Mobility Control in a Layered, 2D Heterogeneous Sandpack[J]. SPE Journal, 2012, 17(04): 1,207-1,220.

[9] Somasundaran P, Huang L. Adsorption/aggregation of surfactants and their mixtures at solid–liquid interfaces [J]. Advances in colloid and interface science, 2000, 88(1): 179-208.

[10] Goldsipe A, Blankschtein D. Molecular-thermodynamic theory of micellization of multicomponent surfactant mixtures: 2. pH-sensitive surfactants [J]. Langmuir, 2007,

23(11): 5953-5962.

[11] Zhou, Z. A., Hussein, H., Xu, Z., Czarnecki, J., & Masliyah, J. H.. Interaction of ionic species and fine solids with a low energy hydrophobic surface from contact angle measurement[J]. Journal of colloid and interface science, 1998, 204(2): 342-349.

[12] Honciuc, A., Baptiste, D. J., & Schwartz, D. K.. Hydrophobic interaction microscopy: mapping the solid/liquid interface using amphiphilic probe molecules [J]. Langmuir, 2009, 25(8): 4339-4342.

[13] Wang, J., & Zhou, X. W.. Syhthesize technics of dodecyl-2-hydroxy-1-proply sulfobetaine [J]. Journal of Shaanxi University of Science & Technology, 2007, 25(2):86-89.

[14] Li, N., Zhang, G., Ge, J., Luchao, J., Jianqiang, Z., Baodong, D., & Pei, H.. Adsorption behavior of betaine-type surfactant on quartz sand [J]. Energy & Fuels, 2011, 25(10): 4430-4437.

[15] Nieto-Alvarez, D. A., Zamudio-Rivera, L. S., Luna-Rojero, E. E., Rodríguez-Otamendi, D. I., Marín-León, A., Hernández-Altamirano, R., ... & Chávez-Miyauchi, T. E.. Adsorption of Zwitterionic Surfactant on Limestone Measured with High-Performance Liquid Chromatography: Micelle–Vesicle Influence [J]. Langmuir, 2014, 30(41): 12243-12249.

[16] Zhang R, Somasundaran P. Advances in adsorption of surfactants and their mixtures at solid/solution interfaces [J]. Advances in colloid and interface science, 2006, 123: 213-229.

[17] Chen, L., Zhang, G., Wang, L., Wu, W., & Ge, J.. Zeta potential of limestone in a large range of salinity [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, 450: 1-8.

[18] Vdović N, Biščan J. Electrokinetics of natural and synthetic calcite suspensions [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 1998, 137(1): 7-14.

[19] Thompson D W, Pownall P G. Surface electrical properties of calcite [J]. Journal of colloid and interface science, 1989, 131(1): 74-82.

[20] Hu, X., Li, Y., Sun, H., Song, X., Li, Q., Cao, X., & Li, Z.. Effect of divalent cationic ions on the adsorption behavior of zwitterionic surfactant at silica/solution interface [J]. The Journal of Physical Chemistry B, 2010, 114(27): 8910-8916.

[21] Zhang P, Tweheyo M T, Austad T. Wettability alteration and improved oil recovery in chalk: The effect of calcium in the presence of sulfate [J]. Energy & fuels, 2006, 20(5): 2056-2062.

[22] Pierre, A., Lamarche, J. M., Mercier, R., Foissy, A., & Persello, J.. Calcium as potential determining ion in aqueous calcite suspensions [J]. Journal of dispersion

science and technology, 1990, 11(6): 611-635.