Solubility of Sodium Dodecyl Sulfate near Propane and Carbon Dioxide Hydrate-Forming Conditions

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The solubility of sodium dodecyl sulfate (SDS) in water at temperatures between (270.5 and 281.3) K near propane and carbon dioxide hydrate-forming conditions was determined by directly sampling the SDS solution from a high-pressure reactor. The SDS solubility near propane or carbon dioxide hydrate-forming conditions is identical to that at ambient conditions. The results indicate that the Krafft point for SDS does not shift to a temperature below 281 K even in the presence of high-pressure propane or carbon dioxide.

Introduction

Gas hydrates are nonstoichiometric crystalline compounds in which hydrogen-bonded water cavities encage small molecules such as methane, ethane, propane, carbon dioxide, and so on.[1] A unit volume of methane hydrates can contain over 160 standard state volumes of gas, and this gas storage capacity is 25 % of the volumetric capacity of liquefied methane at 112 K and is comparable to compressed methane gas at a pressure of 20 MPa.[2−4] Storage of natural gas in hydrate forms also offers a safe and economical feature because natural gas hydrates can form at (270 to 275) K and (3 to 4) MPa and can be stored at the atmospheric pressure and at a typical temperature of 258 K.[5] Despite these merits provided by gas hydrates, one main obstacle to the application of gas storage in clathrates is a low formation rate of gas hydrates with unconverted entrapped water.[6,7]

To overcome these problems, certain surface-active agents have been employed to enhance the rate of hydrate nucleation and hydrate growth.[6,8−12] Among the surfactants investigated, sodium dodecyl sulfate (SDS) was found to be one of the effective additives for maximizing methane storage as well as accelerating the formation rate of methane hydrates.[10,11] In a previous work,[6] the critical micelle concentration (CMC) for SDS was determined as 0.84 mmol·L^{-1} (242 mg·kg^{-1}) in the metastable region of ethane hydrates based on the plot of induction time versus SDS concentration. The formation of SDS micelles may accelerate the growth rate of ethane hydrates because they could act as hydrate nucleation sites.[6] Sun et al.[13] measured the surface tension of SDS solution in contact with methane at pressures ranging from (2.2 to 7.2) MPa, and they determined that the CMC for SDS is about 1.73 mmol·L^{-1} (500 mg·kg^{-1}) at 273.2 K by locating the abrupt change in the slope of the plot of surface tension against SDS concentration.

At temperatures below the Krafft point, the solubility of an anionic surfactant is too low to form micelles in the aqueous phase.[14] The Krafft point is “the temperature (more precisely, narrow temperature range) above which the solubility of a surfactant rises sharply and at this temperature the solubility of the surfactant becomes equal to the CMC”, which is usually determined by locating the abrupt change in the slope of the logarithmic plot of SDS solubility versus temperature.[15] The reported Krafft point for SDS in water ranges from (281 to 289) K at the atmospheric pressure,[16] which is higher than either the temperatures of (275 to 278) K at which ethane hydrates formed[6] or the temperature of 273.2 K at which the surface tension of SDS solutions in contact with methane was measured.[13] Therefore, the studies of Zhong and Rogers[6] and Sun et al.[13] suggest that hydrate formers such as methane and ethane shift the Krafft point for SDS to a lower temperature. The change in the Krafft point for SDS would indicate that the relationship between solubility and temperature is dependent on either the presence or the pressure of hydrate formers.

On the other hand, some previous works[15,17,18] indicated that the presence of high-pressure hydrate formers cannot shift the Kraff point to lower temperatures. However, they presented three SDS solubility data at only two temperatures (at (275 and 279) K), and these experimental results may not support their argument of the unchanged SDS Krafft point. Watanabe et al.[15] reported that the SDS solubility at 279 K in the metastable region of HFC-32 (CH_2F_2) is below 7 mmol·L^{-1} (2000 mg·kg^{-1}), which is less than that ((2200 to 2300) mg·kg^{-1}) at 275 K in the metastable region of methane hydrates.[17,18] They also found that the SDS solubility at 293 K and under 0.101 MPa air is around 7.6 mmol·L^{-1} (2200 mg·kg^{-1})[15] which is very close the SDS solubility at 275 K at methane hydrate-forming conditions, suggesting that SDS may form micelles under these conditions even if they reported that SDS cannot form micelles.[15,17,18] The SDS solubility data have some experimental errors associated with their measurement techniques (indirect methods through water conductivities and surface tension measurements[17,18]). Our recent work confirmed[19] that neither the presence nor the pressure of methane has a significant effect on the solubility of SDS at a wide range of temperatures (270 to 282) K, demonstrating that the Krafft point for SDS in the metastable region of methane hydrates is the same as that at normal ambient conditions.

At present, the solubility of SDS in the metastable region of other gas hydrates except for methane hydrates is less studied.

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Propane hydrates form sII hydrates at a moderate pressure (0.17 MPa at 273.2 K[1]), and methane hydrates form sI at 2.64 MPa and 273.2 K.[1] Carbon dioxide dissolves in water more readily than propane or methane and gives a weak acidic environment when it dissolves in the aqueous phase. Carbon dioxide hydrates form around 1.3 MPa and 273.2 K.[1] The objectives of this paper are to obtain the SDS solubility data in a wide range of temperatures with these two hydrate formers and to give insights into whether or not different guest molecules can cause different SDS solubility. We will measure the solubility of SDS in water at temperatures of (270.5 to 281.3) K by directly sampling the SDS solution through a filter inside a high-pressure reactor in the presence of propane and carbon dioxide. The results presented in this study will clarify whether the different hydrate formers can shift the SDS Krafft point to a lower temperature in the metastable region of gas hydrates.

Experimental Section

Materials. Sodium dodecyl sulfate (SDS) with a certified purity of > 99 % was purchased from Sigma-Aldrich. Propane used in this experiment has a purity of 99 % that was supplied by T. W. Smith. Carbon dioxide was purchased from T. W. Smith with a minimum purity of 99 %. All chemicals were used as received without further purification. Deionized water was produced in our lab with a resistivity of 17 $\text{m}\Omega\cdot\text{cm}^{-1}$.

Apparatus. The experimental apparatus used in this work for directly measuring the solubility of SDS near propane and carbon dioxide hydrate-forming conditions is the same as that used in our previous study to measure the aqueous SDS concentration in the meta-stable region of methane hdyrates.[19] The stainless steel reactor is equipped with two view windows manufactured by Parr Instrument and can be operated at temperatures down to 253 K and at pressures up to 18 MPa. The volume of the reactor including the void space of fitting is 474 mL. The pore diameter of the filter installed inside the reactor is 0.5 μm (NUPRO, SS-4F-K4-05) to strain any SDS precipitates. The temperature of the reactor is controlled by circulating the coolant from an Isotemp 3006P thermostat (Fisher Scientific) with a stability of ± 0.01 K inside the jacket around the cell. The temperature of the liquid phase was monitored with a Type T thermocouple (Omega Engineering); the uncertainty of the temperature measurement in the thermocouple is ± 0.2 K. The pressure of the reactor is measured by using a 9001PDM pressure transducer (Ashcroft, (0 to 34.47) MPa) with the uncertainty of ± 0.05 MPa. Reactor temperature and pressure are sampled every 20 s by the Labview interface.

Procedures. The reactor was first filled with 250 mL of 17.3 $\text{mmol}\cdot\text{L}^{-1}$ (5000 $\text{mg}\cdot\text{kg}^{-1}$) SDS solution and then was purged with the tested gases twice at room temperature. The reactor was pressurized with the tested gases to the desired pressure, followed by setting the temperature of the thermostat to 276.2 K. After visual observation of SDS crystals in the reactor for 1 h, the temperature of the reactor was set to the desired value between (270.5 and 281.3) K and the system was maintained at this temperature for at least (2 to 6) h before sampling the SDS solution. Two samples of (5 to 10) mL of liquid were consecutively taken from the reactor, and only the second sample was analyzed. We analyzed the second sample because the SDS cake builds on the filter during the first sampling and the small SDS particles cannot pass through the filter possibly due to the reduced pore size of the filter during the second sampling. No dramatic change in pressure or temperature was observed just before sampling in all runs. The solubility of SDS at the atmospheric pressure was determined by sampling the SDS solution through a 0.5 μm filter (Whitman Autovial) from a beaker placed in the thermostat.

Table 1. Summary of Solubility of SDS *s* near Hydrate-Forming Conditions and at the Atmospheric Pressure

	T/K	P/MPa	$P/P_{\text{diss.}}$[a]	$s/\text{mmol}\cdot\text{L}^{-1}$
propane	270.5	0.40	2.67	4.80 ± 0.09
	272.3	0.42	2.63	5.09 ± 0.07
	274.4	0.46	2.09	4.99 ± 0.11
	276.3	0.49	1.48	5.51 ± 0.09
	278.5	0.51	0.96	5.93 ± 0.08
carbon dioxide	270.5	1.35	1.32	4.44 ± 0.08
	272.3	1.03	0.94	4.80 ± 0.10
	274.3	3.47	2.43	4.96 ± 0.09
	276.7	3.70	1.57	5.42 ± 0.10
	278.2	4.12	1.83	5.89 ± 0.08
	281.3	3.14	0.95	7.97 ± 0.13
air	270.1			5.09 ± 0.11
	272.0			4.81 ± 0.12
	273.9			5.11 ± 0.15
	275.8			5.68 ± 0.11
	277.8			6.14 ± 0.11
	280.6			7.25 ± 0.13

[a] The dissociation pressure predicted by CSMHYD.[1]

SDS Concentration Analysis. In this study, the saturated SDS concentration in the aqueous phase was determined by titrating the sample with Hyamine 1622 titrant (Omega Engineering). The titration process was monitored by an ISE-8882 surfactant electrode (Omega Engineering), and the endpoint was determined from the first differential plots of the potential versus volume of titrant added.[20] The concentration of SDS was calculated from the volume of titrant added at the endpoint

$$C = C_{\text{titrant}} \frac{V_{\text{titrant}}}{V} \tag{1}$$

Here, C is the concentration of SDS in the aqueous phase; V is the volume of sample; C_{titrant} is the concentration of titrant; and V_{titrant} is the volume of titrant added at the endpoint. The uncertainty of SDS solubility, using this method, is within ± 0.15 $\text{mmol}\cdot\text{L}^{-1}$ (43 $\text{mg}\cdot\text{kg}^{-1}$).

Results and Discussion

The solubilities of SDS in water at temperatures ranging from (270.5 to 281.3) K near propane and carbon dioxide hydrate-forming conditions are summarized in Table 1. The results are also plotted in Figures 1 to 3.

The SDS solubility at temperatures of (270. 5 to 278.5) K is independent of either the pressure or the presence of propane near propane hydrate-forming conditions because the solubility is almost identical to that at atmospheric environments as shown in Figure 1. The solubility does not increase dramatically as temperature increases except for approaching the lowest temperature of the normal Krafft point of (281 to 289) K. This indicates that the Krafft point for SDS at propane hydrate-forming conditions does not shift to a temperature below 281 K. Gayet et al.[21] found that the growth rate of propane hydrates at 274 K and 0.4 MPa maintains a high value until 97 % water is converted to hydrates with an initial SDS concentration of 0.03 $\text{mmol}\cdot\text{L}^{-1}$ (10 $\text{mg}\cdot\text{kg}^{-1}$), which is well below the CMC for SDS at normal ambient conditions. The results presented here indicate that the accelerated effect of SDS on propane hydrate formation is not due to the presence of SDS micelles in the aqueous phase.

The presence of carbon dioxide as well as the pressure of carbon dioxide have no significant effect on the SDS solubility in liquid water at temperatures between (270. 5 and 281.3) K

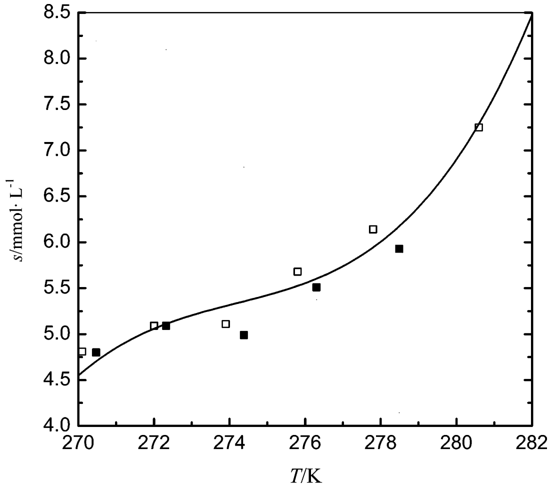

Figure 1. Solubility of SDS, *s*, near propane hydrate-forming conditions and at the atmospheric pressure: ■, propane; □, atmospheric pressure; −, polynomial fit.

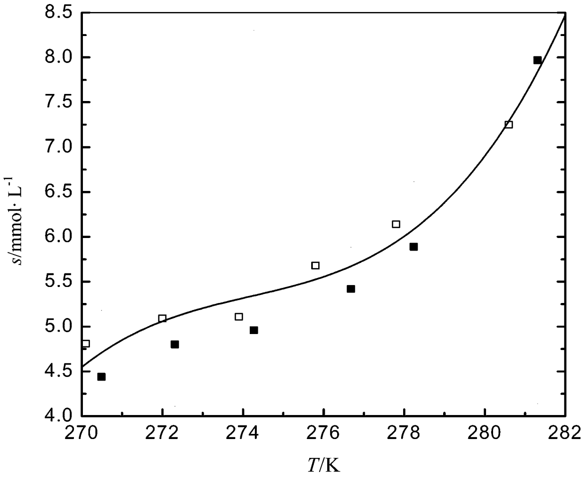

Figure 2. Solubility of SDS, *s*, near carbon dioxide hydrate-forming conditions and at the atmospheric pressure: ■, CO_2; □, atmospheric pressure; −, polynomial fit.

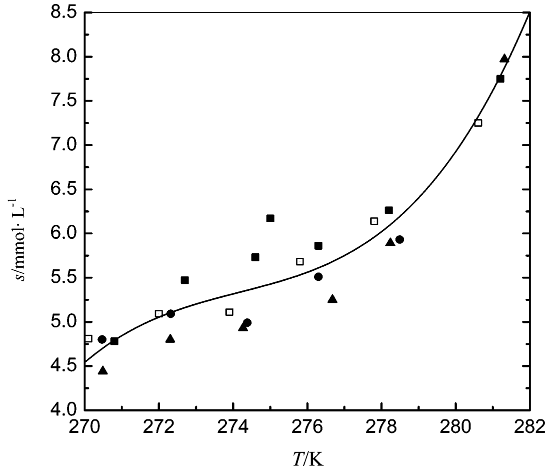

Figure 3. Solubility of SDS, *s*, near methane, propane, and carbon dioxide hydrate-forming conditions and at the atmospheric pressure: ■, methane;[19] ●, propane; ▲, carbon dioxide; □, atmospheric pressure; −, polynomial fit.

near carbon dioxide hydrate-forming conditions as shown in Figure 2. The solubility curve in this plot is almost identical to that of both propane and atmospheric environments in Figure 1, and there is no dramatic increase in the solubility before temperature approaches the lowest temperature of the normal Krafft point (281 K). This also indicates that the Krafft point for SDS at carbon dioxide hydrate-forming conditions does not shift to a temperature below 281 K.

Our previous results[19] and the SDS solubility data presented here indicate that the saturated SDS concentration in the aqueous phase at a temperature range of (270.5 to 281.3) K is independent of the species and the pressure of hydrate formers as shown in Figure 3. The solubility is only a function of temperature. The relationship between the solubility of SDS and temperature is correlated by a third-order polynomial as follows

$$s/\text{mmol}\cdot\text{L}^{-1} = 5.22 + 0.119\cdot(T/\text{K} - 273.1) - 0.0146\cdot(T/\text{K} - 273.1)^2 + 0.00484\cdot(T/\text{K} - 273.1)^3 \quad (2)$$

Conclusions

In this study, the solubilities of SDS in liquid water at temperatures between (270.5 and 281.3) K near propane and carbon dioxide hydrate-forming conditions as well as at atmospheric environments were directly determined by sampling the SDS solution from a high-pressure reactor. The solubility of SDS is independent of either the pressure or the species of hydrate formers, and the relationship between the SDS solubility and temperature in the presence of propane or carbon dioxide at high pressures is identical to that at atmospheric environments. Therefore, the Krafft point for SDS does not shift to a temperature below 281 K, and no SDS micelles are present in the aqueous phase near propane or carbon dioxide hydrate-forming conditions at temperatures below 281 K.

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