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Surfactant effects on hydrate formation in an unstirred gas/liquid system: An experimental study using methane and micelle-forming surfactants

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This paper reports an experimental study in which we intended to obtain a better understanding of the possible role of surfactant micelles on the formation of a clathrate hydrate in a quiescent methane/liquid-water system. The experiments were performed using a laboratory-scale, isobaric hydrate-forming reactor, which was initially composed of a 300-cm^3 aqueous phase and a ~640-cm^3 methane-gas phase, then successively provided with methane such that the system pressure was held constant at 3.9 or 4.0 MPa. The surfactants used in this study were lithium dodecyl sulfate (LDS), dodecylbenzene sulfonic acid (DBSA), and sodium oleate (SO), which have sufficiently low Krafft points and hence, unlike sodium alkyl sulfates (sodium dodecyl sulfate and its homologues), allow the micelle formation under such typical hydrate-forming conditions as those used in this study (~275 K in temperature and 3.9 – 4.0 MPa in pressure). Significant increases in the rate of hydrate formation and the final water-to-hydrate conversion ratio were simultaneously observed by the addition of LDS to the aqueous phase up to concentrations in the range from ~0.6 to ~1.6 times the relevant critical micelle concentration (CMC). Neither the rate of hydrate formation nor the final water-to-hydrate conversion ratio exhibited any appreciable change in the above concentration range. Similar observations were obtained by the addition of DBSA to the aqueous phase up to the concentrations that ranged from ~0.5 to ~2.9 times the relevant CMC. Based on these observations, we have concluded that micelles of LDS and DBSA have no practical effect on hydrate formation. No substantial promotion of hydrate formation was detected by the addition of SO to the aqueous phase up to concentrations that ranged from ~0.8 to ~4.2 times the relevant CMC.

1. Introduction

This study is concerned with the effects of surfactant additives on the formation of a clathrate hydrate (abbreviated hydrate, hereafter) in a system containing an aqueous phase and a methane gas phase in mutual contact. Many studies, mostly experimental studies, have been reported so far about the effects of various surfactant additives on the formation of hydrates, crystalline solid compounds formed from water and various guest substances including light hydrocarbons, carbon dioxide and some fluorocarbons. The fact that the hydrate formation is substantially promoted by the addition of some types of surfactants is of potential importance for the industrial applications of such hydrates, for example, the storage and transport of natural gas or hydrogen, the separation of carbon dioxide from flue gas at coal-fired power plants, the recovery of clean water from the waste water generated at paper-making mills, and the cool storage for residential air conditioning. The point of particular interest in the hydrate formation in surfactant-containing systems is that, even in the absence of any mechanical means for mixing the aqueous and the guest-gas phases inside a hydrate-forming reactor, high-rate hydrate formation continues, generating porous hydrate layers climbing on the wall of the reactor from the level of the horizontal interface between the two fluid phases (Kutergin et al., 1992; Mel'nikov et al., 1998; Zhong and Rogers, 2000; Sun et al., 2003a, 2003b, 2003c; Watanabe et al., 2005a; Pang et al., 2007; Okutani et al., 2007, 2008). If the water (or the aqueous liquid) inside the reactor is not replenished during the hydrate-forming process while the guest gas is continuously replenished (just as in ordinary isobaric, semi-batch hydrate-forming operations), the high-rate hydrate formation lasts until the aqueous phase reduces to ~5 – 20% of its initial volume (Okutani et al., 2007, 2008). These findings indicate the possibility of developing an economical, high-performance industrial hydrate-forming technology utilizing appropriate surfactant additives.

One of the fundamental and, at the same time, practically important question still left for a better understanding about the hydrate formation in surfactant-containing systems is the effect

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of surfactant micelles formed in the aqueous phase on the hydrate-formation kinetics. As surveyed by, for example, Okutani et al. (2008), this issue was once a subject of controversy. Although the controversy is apparently over at present, the issue is still not yet completely settled, which is briefly discussed below. Zhong and Rogers (2000) were probably the first to raise this issue. For interpreting their experimental results about the effect of ethane hydrate formation in the presence of an anionic surfactant, sodium dodecyl sulfate (SDS), they suggested that SDS micelles once formed would work as the carriers of ethane molecules to the bulk of the aqueous phase and thereby promoting the hydrate formation. However, this hypothesis has been disputed and denied by several research groups on the basis of different arguments (Di Profio et al., 2005, 2007; Watanabe et al., 2005a, 2005b; Gayet et al., 2005; Pang et al., 2007; Zhang et al., 2007a, 2007b, 2007c). The most straightforward argument against this hypothesis was probably that micelles could not be formed by many surfactants including SDS at temperatures used in ordinary hydrate-forming operations, i.e., typically less than 283 K (Di Profio et al., 2005; Watanabe et al., 2005a, 2005b; Zhang et al., 2007b, 2007c). That is, the lowest micelle-forming temperature, known as the Krafft point, for each of such surfactants is generally higher than 283 K (Watanabe et al., 2005a). Thus, we can safely claim that the promotion of hydrate formation observed in experimental systems containing SDS or its homologues has no relation to any surfactant micelles. However, the following question still remains unanswered: if micelles were actually formed in a hydrate-forming system containing a low Krafft-point surfactant, how will the hydrate formation be affected? The only previous study concerned with this point was reported by Di Profio et al. (2007). Using an electrical-conductometric technique, they confirmed that three anionic surfactants, dodecylbenzene sulfonic acid (DBSA), sodium oleate (SO) and cetyltripropylammonium bromide (CTPABr), formed micelles in the aqueous phase in contact with methane at a pressure of $p=4$ MPa and temperature of $T=275$ K as far as their initial concentrations in the aqueous phase, c, were in excess of the relevant critical micelle concentrations (CMCs). Unexpectedly, Di Profio et al. (2007) found that, as for DBSA and SO, the hydrate formation in a magnetically stirred reactor was retarded when $c>$ CMC as compared to that in the range of $c<$ CMC. The reduction of hydrate-formation rate in the range of $c>$ CMC was moderate for DBSA, but significant for SO. The effect of CTPABr on the hydrate formation was so low that we could hardly discern any substantial difference between the rates of hydrate formation at $c>$ CMC and $c<$ CMC. Based on such observations, Di Profio et al. (2007) concluded that surfactant micelles do not promote, but inhibit the hydrate formation from methane. Considering that these observations were limited to a specific stirred system and that the mechanism of inhibition has not yet been clarified, we planned this study to observe methane-hydrate formation in an unstirred system containing a micelle-forming surfactant. Except for the selection of the surfactants to use, we performed this study based on the procedure of our previous study of methane-hydrate formation in a surfactant-containing system (Okutani et al., 2008). Our observations obtained in such an unstirred system were significantly different, regarding the effect of surfactant micelles, from those reported by Di Profio et al. (2007).

2. Description of experiments

2.1. Materials

We selected three commercially available anionic surfactants for use in this study. They were lithium dodecyl sulfate (LDS), dodecylbenzene sulfonic acid (DBSA), and sodium oleate (SO). DBSA and SO were two of the three surfactants used in the previous study by Di Profio et al. (2007). We selected them for the purpose of comparing the results of the experiments using the same surfactants and different setup/procedures. The selection of LDS was due to its structural similarity to SDS, the surfactant the most extensively used in previous hydrate studies, and its sufficiently low Krafft point (Smejkal et al., 2003). We expected that the effect of the counterions (Li^+ or Na^+) of the dodecyl sulfate surfactants could be realized by comparing the hydrate formation observed in the presence of LDS to that we previously observed in the presence of SDS using the same experimental apparatus and procedure (Okutani et al., 2008).

The three surfactants were used as received from the suppliers. They were LDS ($C_{12}H_{25}LiO_4S$) having a certified purity of 0.99 in mass fraction (supplied by Nacalai Tesque, Inc., Kyoto), SO ($C_{18}H_{33}NaO_2$) having a certified purity of 0.98 in mass fraction (supplied by Nacalai Tesque, Inc., Kyoto), and DBSA ($C_{18}H_{30}O_3S$) having a certified purity of 0.90 in mass fraction (supplied by Tokyo Chemical Industry Co., Ltd., Tokyo). Each of these chemicals was weighed on an electronic balance (A&D model ER-180A) with a 0.1 mg readability and dissolved in a known volume of deionized and distilled water to prepare each solution sample for the hydrate-forming experiments. The methane used in the experiments was a research-grade gas with a purity of 0.999 in mass fraction supplied by Toyoko Kagaku Co., Tokyo.

2.2. Surfactant concentrations

For each of the three surfactants (LDS, DBSA and SO), we intended to vary the surfactant concentration c in the aqueous solution to be used in each hydrate-forming experiment from run to run over a range extending from the sub-CMC regime to the super-CMC regime. For this purpose, we should know, even roughly, the CMC for each surfactant under the thermodynamic condition to be adjusted in the relevant hydrate-forming experiments, i.e., the condition in which an aqueous phase and a methane-gas phase are in mutual contact at $p=3.9$ or 4.0 MPa and $T=275$ K. Di Profio et al. (2007) reported the CMC values for DBSA and SO determined by electrical conductivity measurements of the solutions in contact with methane gas at $p=4.0$ MPa and $T=275$ K. We recently estimated the CMC values for LDS, DBSA and SO based on our own surface tension measurements using pendant drops suspended in a methane-gas phase adjusted at $p=3.9$ MPa (for LDS) or 4.0 MPa (for DBSA and SO) and $T=275$ K (Ando et al., 2012). The CMC values due to the above two sources are listed in Table 1. Unexpectedly, we find significant disagreements in the CMC values for DBSA and SO between the two sources. Although it is empirically known that surface tensiometry is apt to provide lower CMC values than electrical conductometry (Jana and Moulik, 1991; Das and Das, 2008), the differences between the two sources, particularly that for SO, seem to be too large to be simply interpreted by the above nature of surface tensiometry in comparison to electrical conductometry. This issue has not yet been clarified (Ando et al., 2012). We thus extended the c range of our hydrate-forming experiments for each surfactant such that it safely included, except for SO, the relevant CMC value whichever source we may rely on.[2]

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[2] As for SO, the c range extended up to 100 ppm on the lower side which was not definitely lower than the relevant CMC value due to our surface-tensionmetry-based estimate, 120 ± 30 ppm (Ando et al., 2012). This is because we had planned the hydrate-forming experiments with SO after the CMC value reported by Di Profio et al. (2007) and had finished the experiments before obtaining the relevant surface-tension data by ourselves.