

Viscosity Reduction with Self-Assembly of Cationic Surfactant on Tetra-*n*-butyl Ammonium Bromide Semi-Clathrate Hydrate Aqueous Slurry

Shunsuke Hashimoto^{1*} and Kazushi Kawamura¹

¹*Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan.*

Authors' contributions

This work was carried out in collaboration between all authors. SH designed the study, performed the experiments, wrote the protocol, and wrote all parts of the manuscript. KK assisted the experiments and analyses of the study. All authors read and approved the final manuscript.

Research Article

Received 6th June 2012
Accepted 10th July 2012
Published 18th August 2012

ABSTRACT

Aims: To utilize hydrate slurry for phase change refrigerants, the rheological properties are essential. In the present study, the viscosity characteristics of hydrate slurry are investigated. Additionally, the effect of cationic surfactant on viscosity is also evaluated.

Study Design: Experimental and analytical study.

Place and Duration of Study: Division of Chemical Engineering, Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, between December 2010 and October 2011.

Methodology: Tetra-*n*-butyl ammonium bromide (TBAB) semi-clathrate hydrate aqueous slurry was adopted. The viscosity of solutions and slurries was measured at various concentrations of solution and various solid fractions by use of stress-control-type rheometer. The measurements were performed in the both case without and with cationic surfactant. Additionally, the size and shape and aggregation property of hydrate particles in slurry were evaluated by means of direct observation and zeta potential analysis.

Results: The apparent viscosity of both TBAB solution and hydrate slurry increases as the

*Corresponding author: Email: shunsuke@cheng.es.osaka-u.ac.jp;

temperature decreases, which is caused by the increase of solid fraction in slurry. The TBAB hydrate slurry behaves like pseudo-plastic fluid. In addition, the effect of minimal surfactant on rheological characteristics of TBAB hydrate slurry was investigated. A very small amount of surfactant drastically reduces the apparent viscosity of TBAB hydrate slurry, and then the morphology of TBAB hydrate particle does not change regardless of the existence of surfactant. From the measurement on zeta potential of the surface of TBAB hydrate particle, the viscosity reduction effect may be caused by the electric repulsion of surfactant-adsorbed hydrate particles.

Conclusion: A very small amount of surfactant drastically reduces the apparent viscosity of TBAB hydrate slurry, which is due to the electric repulsion among surfactant-adsorbed hydrate particles.

Keywords: Semi-clathrate; hydrate slurry; viscosity; self-assembly; surfactant; tetra-*n*-butyl ammonium bromide.

NOMENCLATURES

C : concentration, wt%; H_f : hydrate fraction in slurry; m , n : arbitrary real numbers; T : temperature, K; $\dot{\gamma}$: shear rate, s^{-1} ; η : apparent viscosity, Pa•s; τ : shear stress, Pa.

1. INTRODUCTION

Gas hydrates are one of clathrate inclusion compounds, which are stabilized by guest species in the cavity of cages. These hydrate cages are composed of the hydrogen-bonded water molecules. The hydrate structure mainly depends on the size, shape, and physical properties of enclathrated guest species. Generally, the van der Waals interaction (attractive and repulsive forces) operates on the guest and water molecules. That is, the guest molecules engaged in the clathrate hydrate do not participate in forming hydrate lattices (Sloan et al., 2008).

Unlike ordinary gas hydrates, the hydrate formed from tetra-*n*-butyl ammonium salt solution has been known as a semi-clathrate hydrate where the quaternary ammonium cation and anion are incorporated with the hydrogen bonds of water molecules to construct hydrate cages (Mcmullan et al., 1959; Aladko et al., 2002). In addition, four butyl groups are one-by-one engaged with a large cage separately in this semi-clathrate system. Tetra-*n*-butyl ammonium bromide (hereafter, TBAB) hydrate is well known as a semi-clathrate hydrate former. There are various reports about the crystal structure and the role of bromine for the TBAB hydrates (Aladko et al., 2002; Shimada et al., 2003). The hydration numbers of these structures are 26 and 38, which are described as Type A (tetragonal) and Type B (orthorhombic), respectively (Oyama et al., 2005; Shimada et al., 2005). The concentration of aqueous TBAB solutions results in differences of the crystal structure and thermodynamic stability of TBAB hydrate. Recently, TBAB has become the object of much attention as an attractive medium for hydrogen storage and transportation (Hashimoto et al., 2006, 2008).

Recently, slurry with phase change materials (hereafter, PCM) having latent heat have received much attention as a high-density heat transportation system. The utilization of such PCM slurry can reduce flow rate of heat media, since latent heat of some materials is much larger than sensible heat (Darbouret et al., 2005; Kumano et al., 2011; Ma et al., 2010; Song

et al., 2009; Xiao et al., 2006). Fukushima et al. (1999) reported the ability of TBAB semi-clathrate hydrate slurry as latent heat transport media. There is a report (Oyama et al., 2005) about thermodynamic properties such as phase equilibria and dissociation enthalpy of TBAB hydrate. However, there is lack of important information about rheological property of TBAB hydrate slurry for the application to latent heat transport media except for some reports (Darbouret et al., 2005; Kumano et al., 2011; Ma et al., 2010; Song et al., 2009; Xiao et al., 2006). In those previous reports, the fluid property containing apparent viscosity of TBAB hydrate slurry was evaluated by use of the pipe/tube flow apparatus. Unfortunately, discrepancy appeared on the non-Newtonian type of TBAB hydrate slurry according to different authors: Darbouret et al. (2005) and Song et al. (2009) claimed that TBAB hydrate slurry behaves as a Bingham fluid, which indicated that they would behave a Newtonian fluid after overcoming the corresponding yield stress. On the other hand, Xiao et al. (2006) and Kumano et al. (2011) applied the power-law equation to the TBAB hydrate slurry and described them as a shear-thinning pseudo-plastic fluid. Ma et al. (2010) also reported that TBAB hydrate slurry could be treated as a shear-thinning pseudo-plastic fluid except for turbulent flow regions. Of course, the viscosity of hydrate slurry significantly depends on the macroscopic structure of slurry, and then the viscosity and pressure-drop (or friction coefficient) in the internal flow (that is, the flow in tube or duct should have the engineering importance). However, it is scientifically important to investigate the behavior of TBAB hydrate slurry containing accurate viscosity and particle morphology by use of rheometer with the more microscopic view.

In addition, the slurry containing small particles generally have high viscosity, which causes significant energy loss in transportation. Consequently, this cancels the effect of flow rate reduction. To solve this problem, the drag reduction technology with a small amount of cationic surfactant can be applied. The mechanism of drag-reduction occurrence with surfactants has been still discussed by many researchers. In such a surfactant solution, the rod-like micelles of surfactant molecules form and then they form a kind of network structures under the conditions of shear addition. This high-order micellar structure called as shear induced structure (hereafter, SIS) causes shear-thickening of apparent viscosity and adds visco-elasticity to the fluid. Many researchers believed that the existence of SIS in solution was related to the drag-reduction occurrence (Ohlendorf et al., 1986; Qi et al., 2002). Under the existence of hydrate particles, however, there may be some interactions between hydrate particle or guest species and surfactants. In fact, although there are a few reports on the drag reduction of hydrate slurry using surfactants (Suzuki et al., 2006, 2009), the detail mechanism is still unclear.

In the present study, first of all, the viscosity characteristics of TBAB solutions and hydrate-slurry containing Type A crystal were measured at various concentrations of TBAB solutions by use of a stress-control-type rheometer with parallel-plate device. In addition, the effect of a cationic surfactant on the rheological characteristics of TBAB hydrate slurry was investigated by means of zeta potential analysis.

2. EXPERIMENTAL DETAILS

2.1 Apparatus and Procedures

The viscosity characteristics of TBAB solution and hydrate slurry under various temperature conditions were measured by use of stress-control-type rheometer (Physica MCR 302, Anton Paar, Ltd.). A parallel plate device with 50 mm diameter and 1 mm gap between two

plates was applied. The shear rate, $\dot{\gamma}$ ranged from 1 to 2000 s^{-1} and the fluid temperature was controlled by a Peltier device and ranged from 276 to 284 K. The availability of this parallel plate device for the viscosity measurements of solid-solution slurry at least in the range of $\dot{\gamma} < 2000 \text{ s}^{-1}$ was confirmed in the previous study (Suzuki et al., 2006). Firstly, the TBAB solution prepared at a desired concentration was set on the plate of rheometer. Then, the rotation of upper plate was started at a desired speed. At the same time, the temperature of lower plate was cooled down to a desired temperature (sub-cooling degree, $\Delta T = 3 \text{ K}$ from the equilibrium temperature of corresponding TBAB hydrate). Then, the contents were stimulated with a spatula to support nucleation. Therefore, the nucleation was not stochastic in this case. Then, the formation of TBAB hydrate could be confirmed with the drastic increase of apparent viscosity and a small rising of system temperature (because the hydrate formation was exothermic reaction). After that, the temperature was kept for about 3 min to stabilize the hydrate fraction in slurry. After the system reached a steady state, the viscosity measurements were started. In the present study, the shear stress was maintained for at least 3 min to obtain accurate viscosity data. It was confirmed that after 3 min since hydrate formation started (except for the induction period of hydrate formation), the average diameter (mean size) of hydrate particles became steady and then the viscosity value exhibited corresponding constant value. This may be due to the small amount of contents and uniform shear rate in the vertical direction (the gap of two plates is at most 1 mm and there is almost no boundary layer) unlike the other previous reports. In the present study, the reproducibility of data has been confirmed successfully under high shear-rate conditions. One the other hand, the fluid is easy to become inhomogeneous because the larger size particles are apt to deposit to the bottom. Consequently, it is difficult to measure reproducible viscosity data particularly under low shear-rate conditions. In the present study, we came up with an appropriate technique so that the particle-size distribution did not affect the viscosity data under low shear-rate conditions. In this case, at first, the slurry contents were dispersed at the high speed of plate rotation. After that, the rotational speed was set a desired low shear-rate. Then, the viscosity value became high drastically and was maintained for a while. Finally, the apparent viscosity gradually became lower and lower because the hydrate particles started sinking. Thus, we can obtain the reproducible data before the sinking of hydrate particles. The resolution of shear stress was 0.001 Pa. During measurements, the fluctuation of data was at most 0.05 Pa, and then the maximum uncertainty of experimental measurements was within $\pm 0.05 \text{ Pa}$. Incidentally, the reproducibility of measurements was confirmed by repeating same measurements three times using fresh aqueous solution.

The zeta potential of the TBAB hydrate particles in their slurry (average particle size of TBAB hydrate was controlled to ca. 0.050 μm) was measured by use of zeta potentializer (Zeta PALS, Nikkiso, Co., Ltd.) in the both cases with and without surfactant. In advance, the TBAB hydrate particles were prepared by agitating 20 wt% TBAB solution appropriately at ca. 281 K, which was close to the equilibrium temperature. After being annealed at 281 K for a few hours, a small amount of slurry was sampled and its zeta potential was measured. At the same time, a small amount of slurry was observed by use of CCD camera and then it was confirmed that the average particle diameter of TBAB hydrate particle was ca. 0.050 μm .

Fig. 1 shows the thermodynamic stability of Type A TBAB hydrate (temperature – composition diagram) at atmospheric pressure with the existence of air (Fukushima et al., 1999; Hashimoto et al., 2008). The TBAB hydrate is stable at the temperatures below the line that is equivalent to the stability boundary of TBAB hydrate. In other words, TBAB hydrates dissociate at the temperatures above this equilibrium line. As shown in Fig. 1, the

stoichiometric concentration of tetragonal TBAB hydrate is 40.5 wt% where the TBAB hydrate can be stable at ca. 285 K. In the viscosity measurements, four conditions of TBAB concentration in aqueous solution were adopted as follows: 20, 25, 30, and 35 wt%. In the present experimental conditions, only Type A hydrate could be formed, which was preliminarily confirmed based on the Raman spectra of generated hydrate particles. It was confirmed that the T - x diagram (Fig. 1) did not change depending on the contact with air and metal surface. In the present study, the hydrate fraction (mass standard) in slurry, H_f was determined by the following equation:

$$H_f = (C_i - C_{eq}) / (40.5 - C_{eq}) \quad (1)$$

where C_i and C_{eq} stand for the initial concentration of TBAB in aqueous solution and steady concentration of TBAB in the liquid phase of slurry, respectively. Fig. 2 shows the relation between H_f and temperature. The H_f decreases monotonically as temperature rises.

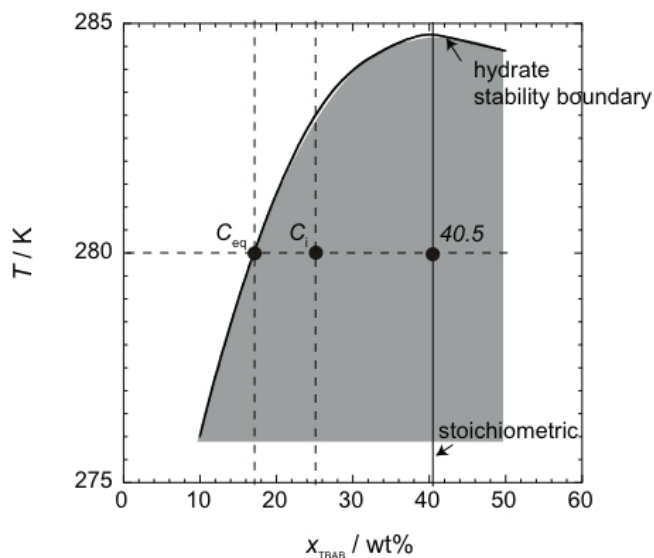


Fig. 1. Temperature – composition diagram for the TBAB + water mixed system containing stability boundary of Type A hydrate (Fukushima et al., 1999; Hashimoto et al., 2008). The gray-colored region stands for the region that TBAB hydrates can be stable

As drag-reducing additives, Ethoquad O/12 was adopted, and sodium salicylate was also added to the solution as a counter ion. The present surfactants were dissolved in distilled water at the concentration of 250, 500 and 1000 ppm (volume ratio) with sodium salicylate of which molar ratio to surfactants was fixed at 1.5 (Suzuki et al., 2006). The solutions with surfactants were allowed to equilibrate at least for one day prior to viscosity measurements. In this case, the concentration of TBAB solution was fixed at 20 wt%. Incidentally, the size of surfactant molecule is too big to occupy hydrate cages. In advance, it was confirmed that the present surfactant concentration had almost no effect on the stability of TBAB hydrate and the equilibrium line of TBAB hydrate was not shifted with this surfactant, although it slightly affected the stochastic induction time of hydrate nucleation and required sub-cooling degree. Hence, the hydrate fraction in the aqueous solution was not also varied.

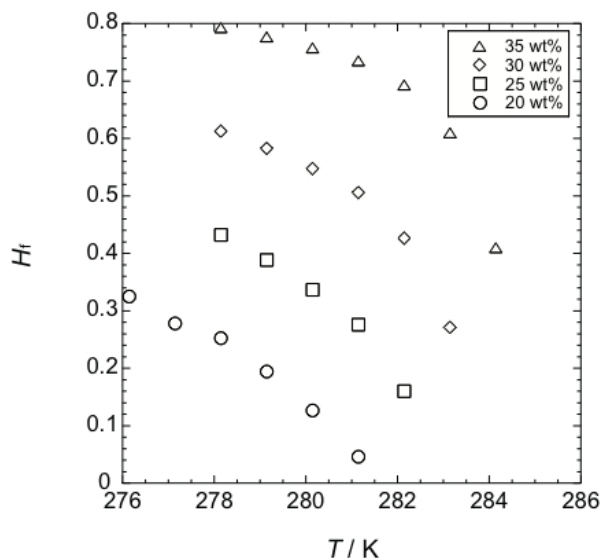


Fig. 2. The relation between hydrate fraction and temperature

2.2 Materials

Research grade TBAB (mole fraction purity 0.980) and sodium salicylate (mole fraction purity 0.950) were obtained from Wako Pure Chemical Industries, Ltd. A cationic surfactant of oleylbishydroxyethylmethylammonium chloride (Ethoquad O/12, $C_{18}H_{35}N(C_2H_4OH)_2CH_3Cl$) was obtained from Lion Akzo Co, Ltd. The distilled water was obtained from the Wako Pure Chemical Industries, Ltd. All of them were used without further purifications.

3. RESULTS AND DISCUSSION

3.1 Viscosity Characteristics of TBAB Aqueous Solution and Hydrate Slurry

First of all, the viscosity of TBAB aqueous solutions (15, 20, 30, and 40 wt%) at various concentrations and temperatures was measured. Fig. 3 shows the viscosity of TBAB solution that is measured during induction period of hydrate formation. As shown in Fig. 3, the apparent viscosity, η_{app} of TBAB solution that is obtained at $\dot{\gamma} = 100 \text{ s}^{-1}$ increases as the temperature decreases and concentration of TBAB in solution increases. In Fig. 3, the data of solution viscosity below the hydration temperature were obtained at sub-cooled states. The viscosity of TBAB solution is several or dozens of times as large as that of water. In addition, as shown in Fig. 4, the TBAB solution behaves as a Newtonian fluid in the shear-rate range of $<ca. 500 \text{ s}^{-1}$. On the other hand, the apparent viscosity of TBAB solution increases gradually in the range of $> 500 \text{ s}^{-1}$. It is also confirmed that this shear-thickening behavior occurs without hysteresis. Since other reference materials (low-viscosity samples such as water and/or NaCl aqueous solution) do not exhibit this shear-thickening behavior in the range of $> 500 \text{ s}^{-1}$, this shear-thickening behavior is not derived from the inertia and/or secondary flows caused by centrifugal force, let alone phase change. Thus, this implies that the conformation change or distortion of butyl groups in TBAB molecules may occur under high-shear conditions, which may be derived from the structural change of local water-

network (Takekiyo and Yoshimura, 2006). It is generally considered that TBAB behaves like a cationic surfactant in aqueous solution. Hence, it is reasonable to guess that TBAB constructs a structure like a SIS of cationic surfactant at high-shear rate (Qi and Zakin, 2002).

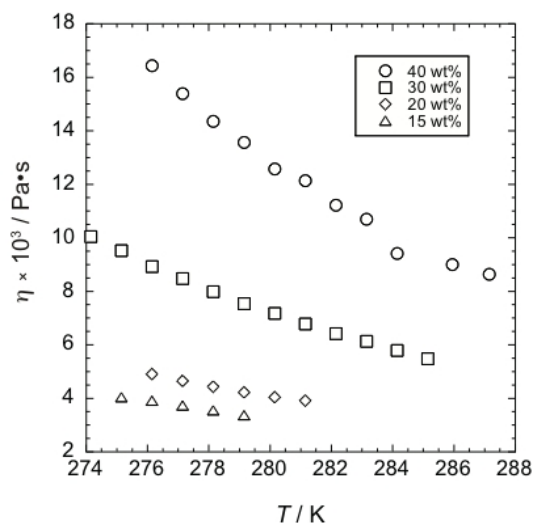


Fig. 3. The temperature variation of apparent viscosity for the TBAB aqueous solutions, which is obtained at the shear rate of 100 s^{-1} .

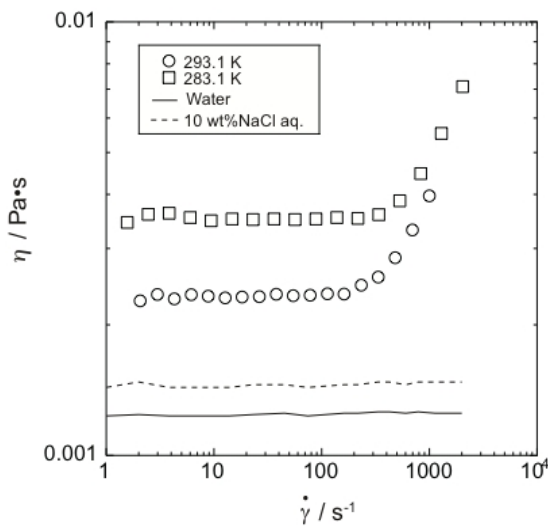


Fig. 4. The temperature dependence of apparent viscosity for the 20 wt% solution. Figure contains the reference data obtained from water and NaCl aqueous solution at 283.1 K

Fig. 5(a) and (b) show the temperature dependence of shear stress and apparent viscosity on TBAB hydrate slurry prepared from 20 wt% aqueous solution, respectively. The average particle diameter of hydrate particles is ca. 0.05 mm, which have a rod-like shape (For detail,

see next section). As shown in Fig. 5(a), the TBAB hydrate slurry behaves as a non-Newtonian fluid like pseudo-plastic fluid without yield stress (for detail, see the expanded view of Fig. 5(a) in the low shear-rate region), which is expressed by the following equation:

$$\tau = -m(d\epsilon/dy)^{n-1}(d\epsilon/dy) = -m\dot{\gamma}^n \quad (2)$$

where m and n stand for fitting parameters of power-law equation. When $n = 1$, the behavior is like Newtonian fluid. This trend is observed in the other cases of various concentrations, while it is confirmed that the yield stress appears at $H_f > 0.5$. This implies the adhesion and aggregation of TBAB hydrate particles with one another under high H_f conditions. The present results are coincident with those of Xiao et al. (2006), Ma et al. (2010), and Kumano et al. (2011), while they do not agree well with those of Darbouret et al. (2005) and Song et al. (2009). Although the occasion on the discrepancy of slurry behavior among those results is still unclear, it is reasonable to guess that the complicated flow distribution in tube or duct causes the complicated movement and interaction among hydrate particles including some stagnation points near the tube wall. In fact, it is pretty difficult and impossible to estimate the accurate overall shear rate from the average velocity in tube or duct. Although the behavior of TBAB hydrate slurry in tube or duct is macroscopically and industrially important, the present evaluation by use of rotational rheometer with the small gap of plates can provide the findings of accurate viscosity with the view of microscopic behavior of slurry. The estimated values of fitting parameters in Fig. 5(a) are summarized in Table 1. At 281.1 K, the hydrate fraction is very small ($H_f = ca. 0.02$) and consequently the hydrate slurry behaves like Newtonian fluid as in the case with aqueous solution (Ma and Zhang, 2012). In addition, as shown in Fig. 5(b), the apparent viscosity of TBAB hydrate slurry increases with the temperature decrease, which is derived from the increase of hydrate fraction (from 0.12 to 0.25). Incidentally, the shear thickening phenomena were not observed till at least 1000 s^{-1} . These results may imply that mean size of hydrate particle does not affect the viscosity under the present experimental conditions.

In fact, as shown in Fig. 6, the apparent viscosity of TBAB hydrate slurry also increases as the concentration of TBAB in aqueous solution becomes higher, where the hydrate fraction increases. In this case, the concentration of aqueous solution in slurry decreases as the hydrate fraction increases. Thus, the viscosity increase with temperature decrease is mainly derived from the increase of hydrate fraction. Although the viscosity properties of non-Newtonian fluids should be generally measured by use of cone-plate-type rheometer because it has homogeneous shear rate in the radius direction, it is quite difficult to measure reproducible viscosity data of solid-liquid slurry by use of cone-plate device. Even if the absolute viscosity value of TBAB hydrate slurry obtained in the present study may be not very important because they are measured by use of parallel-plate device, the viscosity behavior of TBAB hydrate slurry and their characteristics of pseudo-plastic fluid without yield stress are significant for the industrial application.

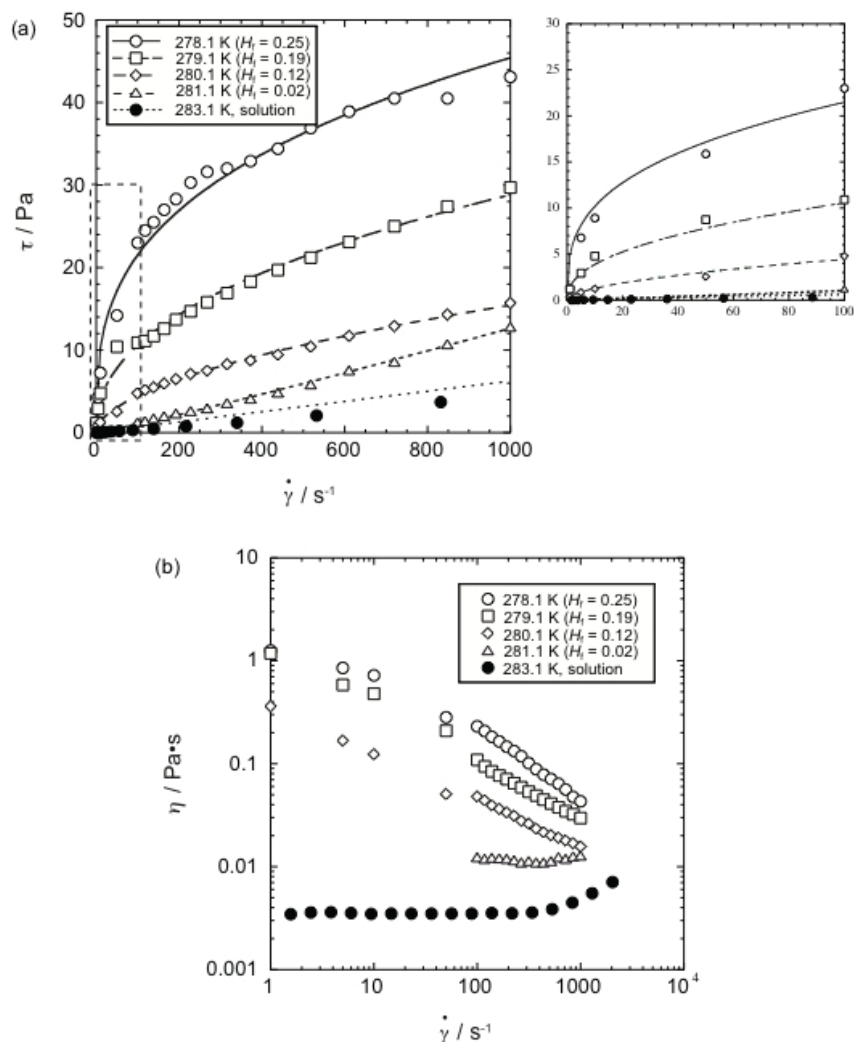


Fig. 5. The temperature dependence of shear stress (a) containing the expanded view of the low shear-rate region ($< 100 \text{ s}^{-1}$) and apparent viscosity (b) for the 20 wt% TBAB solution and hydrate slurry. In panel (a), the lines stand for the fitting curves by use of power function (Eq. 2) except for the case of solution (linear fitting)

Table 1. Fitting parameters for Eq. (2) in Fig. 5(a)

T / K	m	n
278.1	4.808	0.325
279.1	1.414	0.436
280.1	0.363	0.543
281.1	0.007	1.094

*At 281.1 K, the fluid behavior is close to Newtonian fluid.

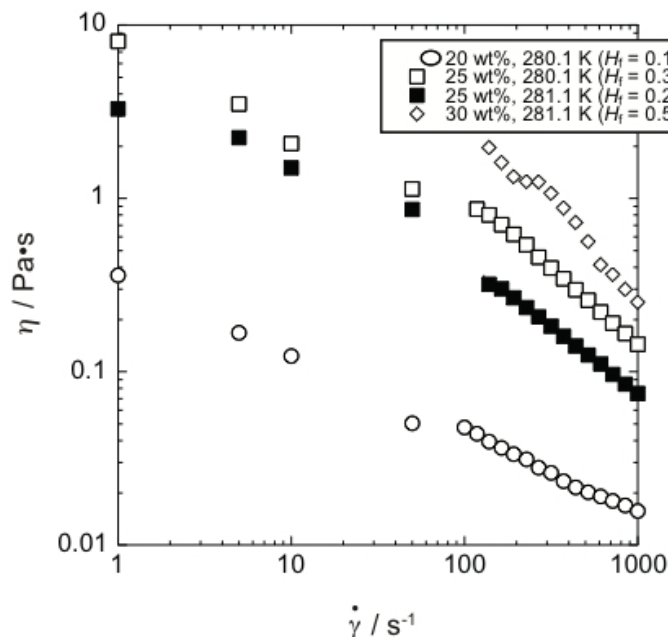


Fig. 6. The TBAB concentration (hydrate fraction) dependence of the apparent viscosity of hydrate slurry

3.2 Effects of Surfactant on Viscosity Characteristics of TBAB Hydrate Slurry

Fig. 7 shows the apparent viscosity of TBAB aqueous solution in the case with surfactant. Obviously, the concentration of surfactant does not affect the viscosity of TBAB solution under less than 500 ppm, while the anomalous viscosity-increase is observed at 1000 ppm. This indicates that the formation of SIS derived from surfactant molecules, which induces the viscosity increase, is not observed under the surfactant concentration is less than 500 ppm. At the surfactant concentration of 1000 ppm, however, the complicated self-assembly of excess surfactant molecules may occur in the aqueous solution.

The surfactant-concentration dependence of the apparent viscosity of TBAB hydrate slurry prepared from 20 wt% aqueous solution is shown in Fig. 8. Regardless of the existence of surfactant, the hydrate slurry behaves like pseudo-plastic fluid. Interestingly, the apparent viscosity decreases drastically compared with those without surfactant in spite of almost the same hydrate fraction. In particular, this trend is remarkable in the region of low shear-stress. In addition, Fig. 8 suggests that the viscosity-reduction effect becomes higher as the surfactant concentration increases under the surfactant concentration is less than 500 ppm. On the other hand, once the surfactant concentration comes close to 1000 ppm, the excess surfactant molecules may form the SIS structure and consequently the viscosity of hydrate slurry increases (the details are discussed later).

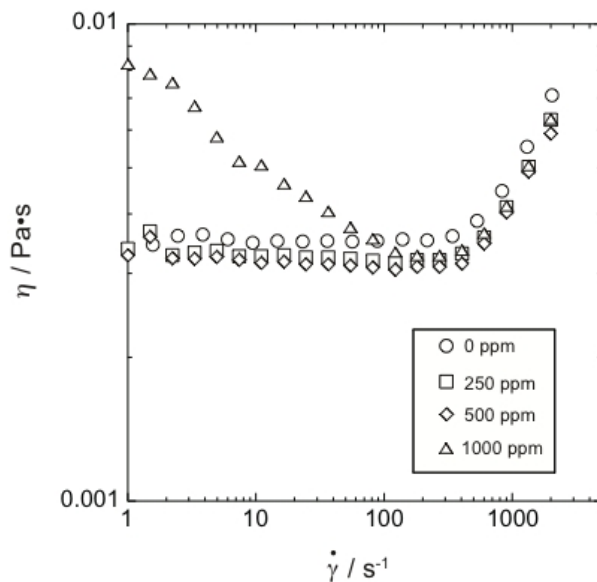


Fig. 7. The apparent viscosity of TBAB aqueous solution (20 wt%) with surfactant (0 ppm means pure TBAB aqueous solution) at 283.1 K

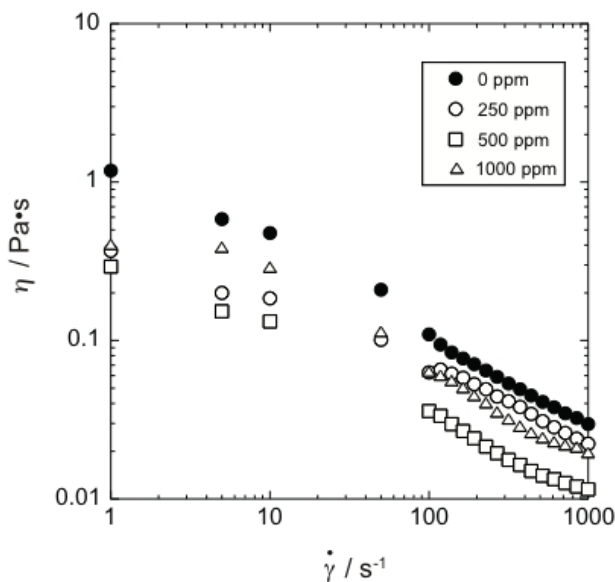


Fig. 8. The surfactant-concentration dependence of apparent viscosity of TBAB hydrate slurry at 279.1 K

Fig. 9 shows the temperature dependence of apparent viscosity of TBAB hydrate slurry prepared from 20 wt% aqueous solution with a small amount (typical result, 250 ppm) of surfactant. Figs. 8 and 9 indicate that there is no difference on the temperature dependence of apparent viscosity between regardless of the existence of surfactant. This implies that surfactants do not affect the whole fluid properties of TBAB hydrate slurry. Incidentally,

similar behaviors were observed in the case of the other concentration of surfactant (500 and 1000 ppm). In addition, in the case with surfactant, the much faster relaxation of apparent viscosity is observed than the case of normal TBAB hydrate slurry when the shear rate is varied periodically, which is similar to the previous study on trimethylolethane hydrate slurry (Suzuki et al., 2006, 2009).

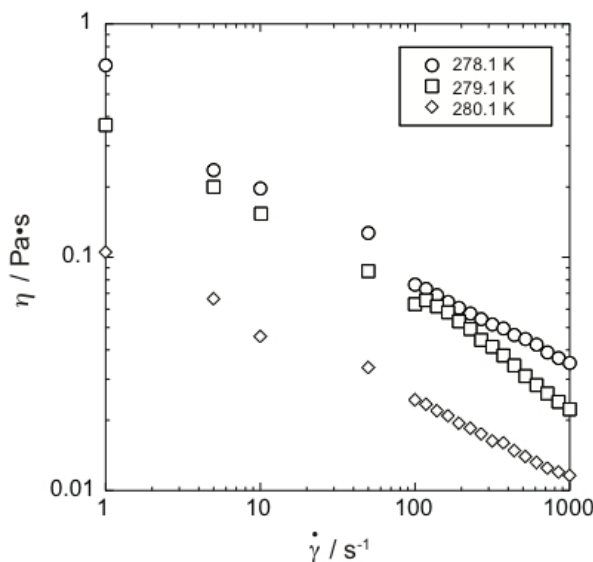


Fig. 9. The temperature dependence of apparent viscosity of TBAB hydrate slurry with surfactant at 250 ppm

In the present study, the average particle size of TBAB hydrate was observed by CCD camera (not in-situ measurements). These particles could be taken out from the rheometer after the apparent viscosity reached at a stable and equilibrium value. The particles were directly sampled from the flow with the same velocity as they were moving in the rheometer. Thus, the process is isokinetically performed. In fact, it was confirmed that the size of hydrate particles did not depend on the time from 3 min to 20 min. Then, they were observed by use of CCD camera controlling the temperature of slurry with a Peltier device. Thus, hydrate particles could not dissociate and it is reasonable to guess that the results obtained by not in-situ observation could be similar to those from in-situ real state. As shown in Fig. 10, TBAB hydrate particles have a rod like structure, while their morphology does not change with the existence of surfactant. Fig. 11 shows the distribution of particle diameter and aggregation frequency of TBAB hydrate particles. In the present study, 500 particles in total were used for analysis. The particle diameter was defined as the major axis of rod-like hydrate particle. In addition, the aggregation particle was defined as the particle that consisted of more than two particles and the agglomeration efficiency was determined as (the number of aggregation particles/the number of total particles). Obviously, the results indicate that the hydrate particle size with surfactant is slightly larger than that without surfactant, while the hydrate particles with surfactant are less subject to aggregation than that without surfactant, which may be derived from the electric repulsion effect with surfactant. According to some previous studies (Nakajima et al., 2008; Peixinho et al., 2010), the morphology of hydrate crystals can affect the rheology of them. In the present study, however, the morphology of TBAB hydrates is not a crucial factor for the viscosity variation depending on surfactant concentration. The diameter of TBAB hydrate particles was at most

several tens of micrometers. The present results demonstrated that not the size and/or morphology of hydrate particle but the solid fraction in hydrate slurry dominantly affected the viscosity characteristics of hydrate slurry under present experimental conditions. In fact, it is confirmed that the yield stress appears at $H_f > 0.5$ in the present study. This implies the adhesion and aggregation of TBAB hydrate particles with one another under high H_f conditions. On the other hand, it is highly probable that the morphology of hydrate particle affects the viscosity of slurry under the conditions of large particle size.

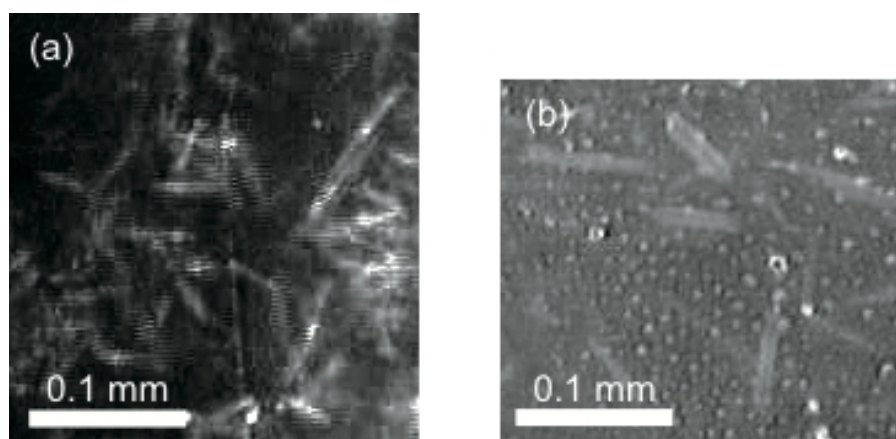


Fig. 10. Typical images of TBAB hydrate particles at 279.1 K ($H_f = ca. 0.15$); (a) without surfactant, (b) with surfactant (500 ppm)

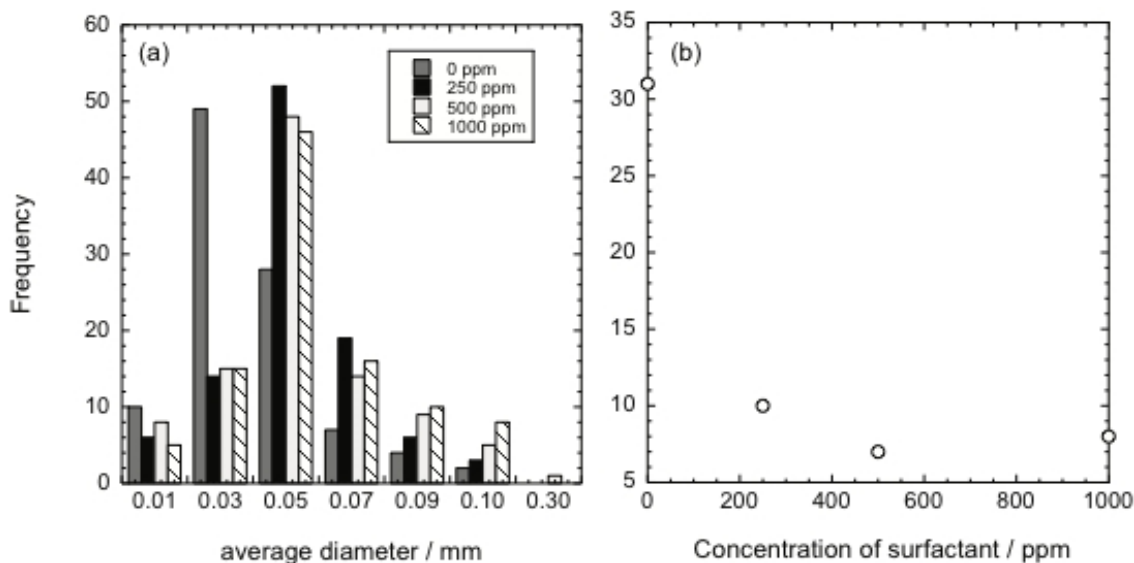


Fig. 11. The dependence of surfactant concentration on particle distribution of TBAB hydrates (a) and their aggregation frequency (b). In panel (a), the aggregation particles are out of consideration

Then, the zeta potential of the TBAB hydrate slurry was measured by use of zeta potentializer under the various conditions with surfactant. As shown in Fig. 12, the zeta

potential of hydrate slurry without surfactant was negative charge and its absolute value was relatively small, while the zeta potential with surfactant exhibits positive and high absolute value. The zeta potential increases with the increase of surfactant concentration under less than 500 ppm, while it is saturated a certain value when the surfactant concentration exceeds 500 ppm. On the other hand, zeta potential at the surfactant concentration of 100 ppm has a certain level of positive value. Thus, it is highly probable that the charge of zeta potential would discontinuously change at a extremely low concentration of surfactant. The results of zeta potential imply the mechanism of viscosity reduction derived from the addition of cationic surfactant, which is summarized in Fig. 13. In the case without surfactant, there is negative charge because of the adsorption of HCO_3^- and Br^- on the hydrate/water surface (Fig. 13a) (Lo et al., 2008). Under the existence of a small amount of cationic surfactant, the species such as HCO_3^- and Br^- also remain at the surface of hydrate particles. Additionally, the hydrophilic headgroups of surfactant, which have positive charge, could cover the hydrate surface homogeneously with the formation of lamella structures (Fig. 13b). As a result, it is suggested that the cohesion or adhesion of hydrate particles may be controlled by the electrical repulsion between adsorbed surfactants and the apparent viscosity may decrease. That is, the results of the measurements on zeta potential of the TBAB hydrate slurry support the electric repulsion effect with surfactant, which is one of the possible reasons for the viscosity reduction with surfactant. In the case that the excess surfactant exists in hydrate slurry, it is likely that the self-assembly of surfactant molecules occurs and then the apparent viscosity of slurry would increase. For the mechanism of viscosity reduction with surfactant, furthermore investigation such as the observation of hydrate surface via cryo-TEM will be required, which may be quite difficult.

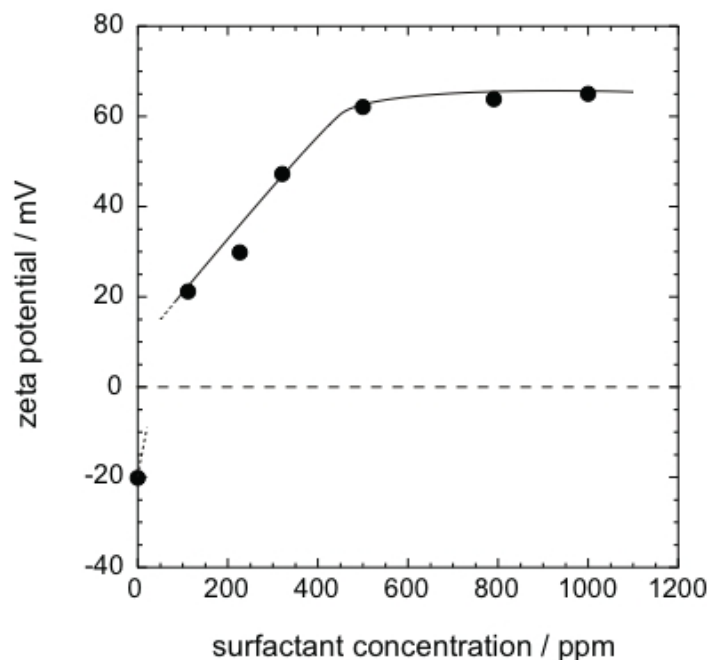


Fig. 12. Zeta potential of TBAB hydrate particles as a function of surfactant concentration

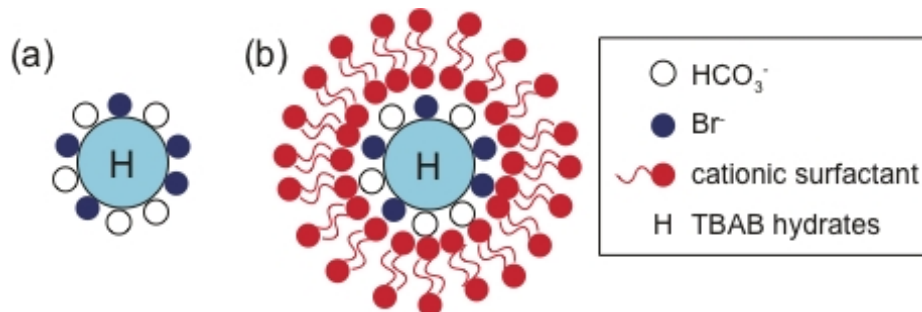


Fig. 13. Schematic illustration of the interaction between TBAB hydrate particles and surfactant molecules; (a) without surfactant, (b) with surfactant

4. CONCLUSION

The viscosity properties of TBAB aqueous solution and hydrate slurry with the existence or nonexistence of surfactant molecules have been investigated by use of rotational rheometer. The important findings are summarized as follows:

1. The TBAB hydrate slurry behaves like pseudo-plastic fluid without yield stress, while the TBAB aqueous solution exhibits the behavior of Newtonian fluid. The apparent viscosity of TBAB hydrate slurry increases as the hydrate fraction increases (the system temperature decreases).
2. The addition of minute cationic-surfactant reduces the apparent viscosity of TBAB hydrate slurry drastically. This viscosity reduction may be derived from the electric repulsion of surfactant-adsorbed hydrate particles.
3. The viscosity reduction effect of cationic surfactant increases as the concentration of surfactant increases, and reaches a plateau value at a certain concentration (500 ppm). At higher concentration than that, the viscosity of hydrate slurry becomes high due to the self-assembly of excess surfactant molecules.

ACKNOWLEDGEMENTS

This work was financially supported by Grant-in-Aid for Scientific Research to S. Hashimoto (Young Research, B, 22760581). The authors thank Prof. Dr. Hiroshi Suzuki and Dr. Yoshiyuki Komoda of Kobe University for the viscosity measurements using rheometer, and Prof. Kazunari Ohgaki and Dr. Takeshi Sugahara for his valuable comments.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

- Aladko, L.S., Dyadin, Yu, A., Rodionova, T.V., Terekhova, I.S. (2002). Clathrate hydrates of tetrabutylammonium and tetraisoamylammonium halides. *J. Struct. Chem.*, 43, 990-994.

- Darbouret, M., Cournil, M., Herri, J.M. (2005). Rheological study of TBAB hydrate slurry as secondary two-phase refrigerants. *Int. J. Refrig.*, 28, 663-671.
- Fukushima, S., Takao, S., Ogoshi, H., Ida, H., Matsumoto, S., Akiyama, T., Otsuka, T. (1999). Development of high-density cold latent heat with clathrate hydrate. NKK Tech.
- Hashimoto, S., Myrayama, S., Sugahara, T., Sato, H., Ohgaki, K. (2006). Thermodynamic and Raman spectroscopic studies on H₂ + tetrahydrofuran + water and H₂ + Tetra-*n*-Butyl ammonium bromide + water mixtures containing gas hydrates. *Chem. Eng. Sci.*, 61, 7884-7888.
- Hashimoto, S., Sugahara, T., Moritoki, M., Sato, H., Ohgaki, K. (2008). Thermodynamic stability of hydrogen + tetra-*n*-butyl ammonium bromide mixed gas hydrate in nonstoichiometric aqueous solutions. *Chem. Eng. Sci.*, 63, 1092-1097.
- Kumano, H., Hirata, T., Kudoh, T. (2011). Experimental study on the flow and heat transfer characteristics of a tetra-*n*-butyl ammonium bromide hydrate slurry (First Report: Flow Characteristics). *Int. J. Refrig.*, 34, 1953-1962.Rep., 166, 65-70 (in Japanese).
- Lo, C., Zhang, J.S., Somasundaran, P., Lu, S., Couzis, A., Lee, J.W. (2008). Adsorption of surfactants on two different hydrates. *Langmuir*, 24, 12723-12726.
- Ma, Z.W., Zhang, P., Wand, R.Z., Furui, S., Xi, G.N. (2010). Forced flow and convective melting heat transfer of clathrate hydrates slurry in tubes. *Int. J. Heat Mass Trans.*, 53, 3745-3757.
- Ma, Z.W., Zhang, P. (2012). Pressure drops and loss coefficients of a phase change material slurry in pipe fittings. *Int. J. Refrig.*, 35, 992-1002.
- Mcmullan, R., Jeffrey, G.A. (1959). Hydrate of the tetra *n*-butyl and tetra *i*-amyl quaternary ammonium salts. *J. Chem. Phys.*, 31, 1231-1234.
- Nakajima, M., Ohmura, R., Mori, Y.H. (2008). Clathrate hydrate formation from cyclopentane-in-water emulsions. *Ind. Eng. Chem. Res.*, 47, 8933-8939.
- Ohlendorf, D., Interthal, W., Hoffmann, H. (1986). Surfactant systems for drag reduction: physico-chemical properties and rheological behaviour. *Rheol. Acta*, 25, 468-486.
- Oyama, H., Shimada, W., Ebinuma, T., Kamata, Y., Takeya, S., Uchida, T., Nagao, J., Narita, H. (2005). Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid Phase Equilib.*, 234, 131-135.
- Peixinho, J., Karanjkar, P.U., Lee, J.W., Morris, J.F. (2010). Rheology of hydrate forming emulsions. *Langmuir*, 26, 11699-11704.
- Qi, Y., Zakin, J.L. (2002). Chemical and rheological characterization of drag-reducing cationic surfactant systems. *Ind. Eng. Chem. Res.*, 41, 6326-6336.
- Shimada, W., Ebinuma, T., Oyama, H., Kamata, Y., Takeya, S., Uchida, T., Nagao, J., Narita, H. (2003). Separation of gas molecules using Tetra-*n*-butyl ammonium bromide semi-clathrate hydrate crystals. *Japanese J. Appl. Phys.*, 42, 129-131.
- Shimada, W., Shiro, M., Kondo, H., Takeya, S., Oyama, H., Ebinuma, T., Narita, H. (2005). Tetra-*n*-butylammonium bromide-water (1/38). *Acta Cryst. C*, C61, o65-o66.
- Sloan, E.D., Koh, C.A. (2008). *Clathrate Hydrates of Natural Gases*. 3rd ed.; CRC Press, Boca Raton: New York.
- Song, W.J., Xiao, R., Huang, C., He, S.H., Dong, K.J., Feng, Z.P. (2009). Experimental investigation on TBAB clathrate hydrate slurry flows in a horizontal tube: Forced convective heat transfer behaviors. *Int. J. Refrig.*, 32, 1801-1807.
- Suzuki, H., Itotagawa, T., Indartono, Y.S., Usui, H., Wada, N. (2006). Rheological characteristics of trimethyloethane hydrate slurry treated with drag-reducing surfactants. *Rheol. Acta*, 46, 287-295.
- Suzuki, H., Wada, N., Komoda, Y., Usui, H., Ujiie, S. (2009). Drag reduction characteristics of trimethyloethane hydrate slurry treated with surfactants. *Int. J. Refrig.*, 32, 931-937.

- Takekiyo, T., Yoshimura, Y. (2006). Raman spectroscopic study on the hydration structures of tetraethylammonium cation in water. *J. Phys. Chem. A*, 110, 10829-10833.
- Xiao, R., Wu, S.S., Tang, L.G., Huang, C., Feng, Z.P. (2006). Experimental investigation of the pressure-drop of clathrate hydrate in *Slurry* (CHS) Flow of Tetra-*n*-Butyl ammonium bromide (TBAB) in straight pipe. Proc. 10th Int. Conf. Therm. Energy Storage, NJ, USA.

© 2012 Hashimoto and Kawamura; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.