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Threadlike Micelles Controlling Viscosities of Cement Slurry

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The threadlike micelle of a cationic surfactant: cetyltrimethylammonium chloride (CTAC), containing anionic aromatic substances has been formed with unique rheological properties in strong electrolyte aqueous solutions and slurry using an inorganic powder such as cement. The threadlike micelle can be used as a high-efficiency viscosity agent for cement slurry.

There have been many studies on the properties of threadlike micelles in aqueous solution.[1–12] In recent years, the micelles have been extensively investigated not only by academic chemists but also by industrial scientists, e.g., a certain type of threadlike micelle that reduces the turbulent frictional drag of water is being studied for district heating/cooling systems.[13,14] However, there is still no report on studies of threadlike micelles under the high ionic strength conditions. Furthermore, the properties and applied research of threadlike micelles in slurry applications using inorganic and hydraulic powder have not been reported so far.

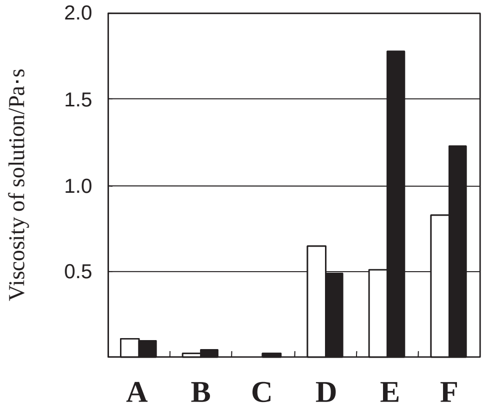

Fig. 1. Viscosity behavior of threadlike micelles in ion exchange water and cement supernatant liquid. A: Cetyldimethylamine oxide, B: Lauramidopropylbetaine/triethanolamine polyoxyethylene (3.0 mol) lauryl ether sulfate, C: CTAC/KBr,[21,23] D: CTAC/sodium salicylate (NaS),[15–20] E: CTAC/sodium *p*-toluenesulfonate (Na*p*TS),[9,10] and F: CTAC/sodium *p*-xylenesulfonate (Na*p*XS). □: Ion exchange water, ■: cement supernatant liquid. Surfactants/0.06 mol L^{-1}.

Table 1. Composition of Cement Supernatant Liquid

Concentration (mmol/L)						pH	I.S.[a]	E.c.[b]
K^+	Na^+	Ca^{2+}	SO_4^{2-}	OH^-	Cl^-			
213	85	18	92	140	5	13.2	444	45.4

a) Ionic strength (mmol/L). b) Electric conductivity (mS/cm).

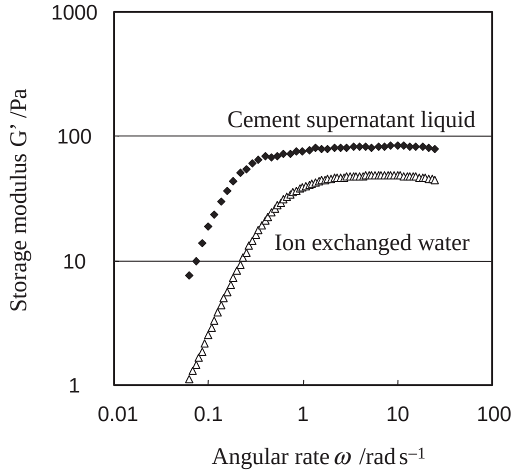

Fig. 2. Dynamic rheology measurements of CTAC/Na*p*TS in ion exchange water (△) and cement supernatant liquid (◆) at the concentration 0.06 mol/L.

In this paper, we report on the general properties of threadlike micelles in strong electrolyte aqueous solutions and cement slurry to develop a novel viscosity agent that can produce cement slurry having stable segregation resistance. Initially, we examined the viscosity behavior of six kinds of threadlike micelles in high ionic strength aqueous solutions (Fig. 1—note: the concentration of surfactants is held constant at 0.06 mol/L). The solvents, ion exchange water, and cement supernatant liquid containing the variety and quantity of inorganic metallic salts which melt out from cement particles were prepared. As the pH of cement supernatant liquid is strongly alkaline, the conditions are quite severe for conventional water-soluble polymers. The analytical values of cement supernatant liquid were measured by inductively coupled plasma spectrometry and ion chromatography (Table 1). Figure 1 shows that the CTAC/anionic aromatic substances, i.e., sodium salicylate (NaS), sodium *p*-toluenesulfonate (Na*p*TS), and sodium *p*-xylenesulfonate (Na*p*XS) exhibited high viscosity in both ion exchange water and cement supernatant liquid at a 1:1 molar ratio. But the viscosities of CTAC/NaS in cement supernatant liquid decreased compared to that in ion exchange water. In contrast, the viscosities of CTAC/Na*p*TS and Na*p*XS increased in cement supernatant liquid. We considered that NaS became less soluble to form salicylate with Ca^{2+} in cement supernatant liquid. It was also thought that it would not be easy for CTAC/NaS to get the most suitable layout to form the threadlike micelle because the hydroxy group of NaS dissociated in cement supernatant liquid of pH 13.2. Dynamic rheology measurements were carried out to investigate the viscosity behavior of CTAC/Na*p*TS in cement supernatant liquid. As shown in Fig. 2, the storage modulus G′ value increases and the plateau is long in cement supernatant liquid as com-

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pared to the results in ion exchange water. This indicates that the intermolecular distance in the micelle is becoming closer due to diminishing intermolecular electric repulsion in the presence of metal ions, so that the threadlike micelle of CTAC/Na*p*TS grows a large network structure. Cement slurry that consists of water (specific gravity 1.00) and cement powder (specific gravity 3.16) exhibits rapid segregation by sedimentation of cement particles. The higher viscosity afforded by the network structure described above lowers the sedimentation velocity of cement particles and the network structure provides enhanced elasticity, giving the slurry a certain level of solid behavior. It therefore becomes possible to prevent segregation of cement slurry significantly by adding the threadlike micelles. Additionally, CTAC/Na*p*XS exhibited a greater viscosity in ion exchange water, while CTAC/Na*p*TS showed higher viscosity than CTAC/Na*p*XS in cement supernatant liquid (Fig. 1). It is thought that the hydrophobic property of the anionic aromatic substance influenced the formation of micelle, in that Na*p*XS tended to become less soluble in cement supernatant liquid because Na*p*XS has stronger hydrophobic property than Na*p*TS. The results for the viscosity of cement slurry (Water 100 g and Cement 100 g mixed) containing the threadlike micelles are shown in Fig. 3. The results of the slurry are reflected in the aqueous solution experiments. CTAC/Na*p*TS exhibited the highest viscosity increase in cement slurry. The slurries of CTAC/NaS, CTAC/Na*p*TS, and CTAC/Na*p*XS were very homogeneous, though segregation was observed in others. It was clear that the threadlike micelle that provides a high viscoelasticity in strong electrolyte aqueous solutions can exhibit excellent segregation resistance in cement slurry. Figure 4 shows the effect of molar ratio of CTAC/Na*p*TS on the viscosity of cement slurry. Na*p*TS exhibited the maximum viscosity at a 1:1 molar ratio. In some studies of aqueous solution, CTAC/anionic aromatic substances exhibit remarkable viscoelastic behavior at a molar ratio of 1:1.[6–8,15] The phenomenon observed in the cement slurry was caused by the property of aqueous solution containing threadlike micelles. In this case, when we measured the adsorption amount of CTAC and Na*p*TS in cement slurry, the adsorption amounts of these were very small, while CTAC/Na*p*TS maintained a 1:1 molar ratio in the water phase of the slurry.

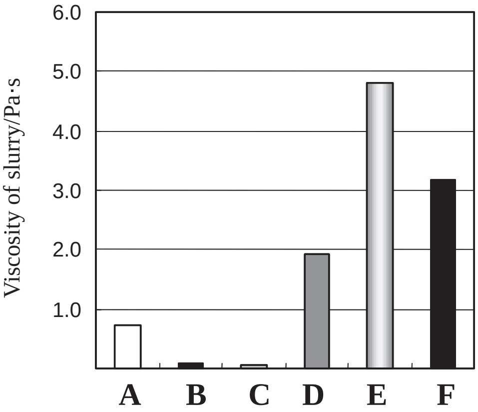

Fig. 3. Viscosity of cement slurry with threadlike micelles added. Cement slurry has water cement weight ratio 1.0. Surfactants/0.06 mol L^{-1}.

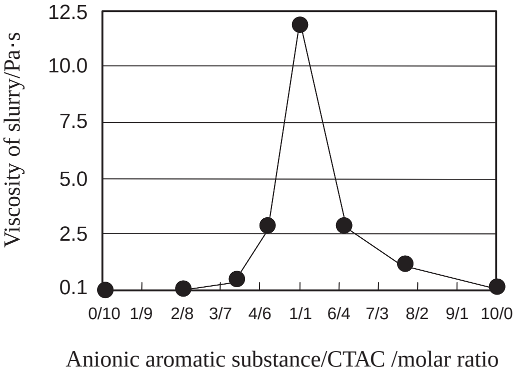

Fig. 4. Effect of molar ratio of CTAC/Na*p*TS on the viscosity of cement slurry. Surfactants/0.12 mol L^{-1}. Water: cement weight ratio 1.0.

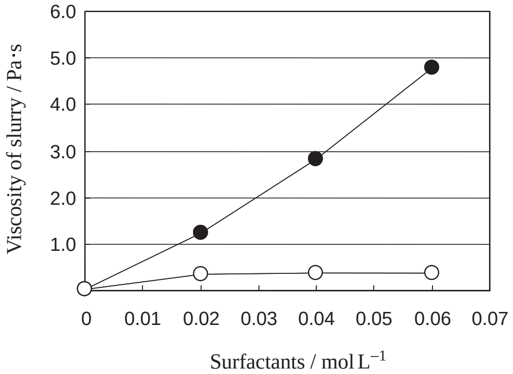

Fig. 5. Viscosity of cement slurry after adding CTAC/Na*p*TS (●) and CTAC/NaBS (○). Water:cement weight ratio 1.0.

Figure 5 shows the effect of anionic aromatic substance chemical structures that have one sulfonic group and one benzene ring with or without one methyl group on the formation of threadlike micelle in cement slurry (CTAC was used). It is clear that the viscosity of CTAC/Na*p*TS cement slurry increases with increasing dosage. Meanwhile, the viscosity of the CTAC/benzenesulfonate (NaBS) cement slurry increases slightly. However, little change is observed with increasing dosage. Additionally, segregation was observed. This suggests that CTAC/NaBS cannot form threadlike micelles of sufficient size, most likely because of lower hydrophobic interaction due to the absence of a methyl group. We measured the methyl group motility of CTAC with Na*p*TS and NaBS by ^{1}H NMR to investigate the influence of the methyl group of aromatic substance on the formation of threadlike micelles (Fig. 6). The proton peak coinciding with the methyl group of CTAC becomes broad when the anionic aromatic substance forms a stable conformation within the micelle and the molecular motion of the methyl group of CTAC is inhibited. Therefore, the half-bandwidth of the peak increases and the interaction between CTAC and anionic aromatic substance can be confirmed. The half-bandwidth results show that the interaction between CTAC and NaBS is not very strong, indicating that it is difficult to form threadlike micelles in cement supernatant liquid.

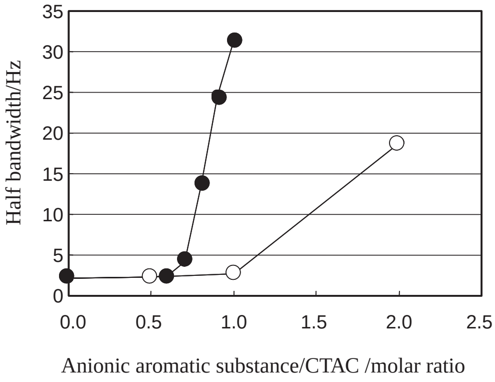

Fig. 6. Methyl group motility of CTAC with Na*p*TS and NaBS by ^{1}H NMR. ●: Na*p*TS, ○: NaBS. CTAC 0.1 mol/L constant.

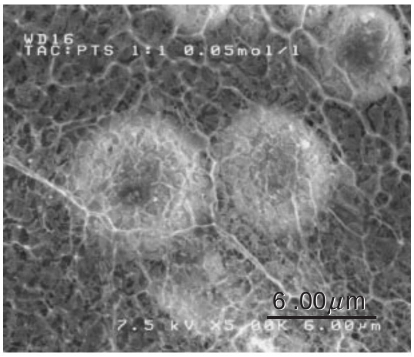

Fig. 7. Cryo-SEM of CTAC/Na*p*TS in slag slurry. Surfactants/0.05 mol L^{-1}.

Finally, Figure 7 shows the picture of the CTAC/Na*p*TS in coexistence with the blast furnace slag powder (mineral composition is very similar to cement) by using Cryo-SEM, CTAC/Na*p*TS of 0.05 mol/L. The threadlike micelle of 30–50 nm in diameter spreads homogeneously around the powder particle. It was reported that the diameter of the threadlike micelle of CTAB (cetyltrimethylammonium bromide)/NaS was about 10–12 nm as determined by TEM at CTAB concentration of 0.001 mol/L.[8,22] We believe that the difference was caused by the influence of CTAC/Na*p*TS concentration and/or that the micelles were bundled and overlapped each other due to high concentration in the strong electrolyte aqueous solution.

In summary, the threadlike micelle of CTAC/anionic aromatic substance is formed in strong electrolyte aqueous solutions and cement slurry. It can efficiently exhibit suitable viscosity in these systems and can give very good segregation resistance to cement slurry. Controlling the slurry viscosity by the formation of threadlike micelles is an effective method to prevent segregation for water–inorganic powder slurries.

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