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ORIGINAL CONTRIBUTION

Dispersion behavior of oleic acid in aqueous media: from micelles to emulsions

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Abstract Dispersion behavior of aqueous solutions containing oleic acid (RH), sodium oleate (R^-Na^+), and NaCl was investigated by turbidity and dynamic light-scattering measurements. Changes of the size of scattering particles in solution composed of 1 mM oleic acid and 100 mM NaCl were traced as a function of the degree of ionization α, in terms of radius of the equivalent hydrodynamic sphere. Large associated micelles with a radius of 30 nm appeared by a slight decline of α and existed at α higher than 0.75. They were responsible for the three-phase equilibrium (solution, micelle and aggregated micelle, and acid–soap, $(R^-Na^+)_3RH$) characterized by a constant pH of 9.75. The appearance of a new phase, $(R^-Na^+)_3RH$, contributed to increase both the turbidity and averaged scattering particle size. As the breakdown of the three-phase equilibrium, radius of scattering particles increased significantly. Finally, oleic acid oil droplets were separated from aqueous phase at low α. When the system was buffered by tris(hydroxymethyl)aminomethane (Tris), scattering particles with a weight-averaged hydrodynamic radius of 75 nm existed in a wide range of α from 0.85 to 0.65. In Tris buffered solution, turbidity formation was induced by the increase in the number of aggregated particles.

Key words Oleic acid – sodium oleate – micelle – acid–soap – light-scattering photometry

Introduction

Oleic acid (RH), *cis*-9-octadecenoic acid, is an essential constituent of the biological system to construct the molecular assemblies and to participate in the important metabolic cycles. In addition, oleic acid has been recognized as a useful industrial substance in mining processes and in the food and pharmaceutical industries. Until now, the physicochemical characteristics of oleic acid and its metal salt, such as sodium oleate (R^-Na^+), have long been examined extensively. Complex nature of oleic acid both in the solid and aqueous solution phases arising from unsaturated bond was demonstrated by a variety of investigations. In sodium oleate/oleic acid two component system, complicated phase diagram indicated the formation of the stoichiometric complexes with R^-Na^+/RH ratio of 3/1, 1/1, and 2/3 [1]. It was also reported that sodium oleate forms easily associative micelles with multiple critical micelle concentrations [2].

Acidification of an aqueous sodium oleate solution leads to further complicated situations of the dispersion behavior. The formation of an oil-in-water emulsion consisting of pure oleic acid oil droplets have been suggested based on the solubility vs. pH relationships [3]. However, subsequent H^+-ion titration studies indicated that the dispersion behavior of oleic acid/sodium oleate mixture in aqueous solution was characterized by various aggregated species including sodium oleate micelles, associated micelles, solid sodium oleates, acid–soaps, and pure oleic acid oil droplets [4, 5]. Analyses of micelle and acid–soap formation processes are required to understand the dispersion behavior in aqueous oleate solution [4–8]. Dispersed states in the aqueous sodium oleate solution were changed continuously or discretely with decreasing pH [5]. In the present study, changes in the characteristics of the dispersed particles as a function of pH, or degree of ionization, were traced directly by the dynamic light-scattering measurements. Then finally, the dispersion behavior of heterogeneous aqueous solution containing oleic acid and sodium oleate was systematically examined based on the light-scattering, turbidity, and H^+-ion titration measurements.

Experimental

Oleic acid used in the present experiments was of more than 99.999% purity (Nippon Oil and Fat Co. Ltd.). In the present experiments to prepare the aqueous sample solutions, with proper values of the degree of ionization, containing oleic acid, sodium oleate, and NaCl, previously reported H^+-ion titration curves were used [5]. The degrees of ionization of the sample solution were identified by adjusting the pH value of solution based on the titration curve relating them with pH. The pH adjustments of sample solutions were performed by adding NaOH or HCl aqueous solutions to aqueous NaCl solutions of sodium oleate. In some experiments, appropriate buffer agent, such as tris(hydroxymethyl)aminomethane (Tris), was also employed. A Jasco Ubest-50 Spectrophotometer was used to measure turbidity formation at 350 nm wavelength under regulated temperature at 25 ± 1 °C.

Dynamic light-scattering experiments were carried out on a Malvern System 4700. The incident light source was an argon ion laser (ILT 5000, Ion Laser Technology) operated at 488 nm. The measured scattering angle ranged 30–120° and the output pulses from photomultiplier were analyzed by a correlator (Model 7032, Malvern Instruments Ltd.). The light-scattering measurements were carried out at regulated temperature, 35.0 ± 0.1 °C, to avoid the turbidity formation in sample solutions under some conditions. The obtained normalized correlation function of the scattered electric field, $g(\tau)$, was analyzed with a double exponential decay mode or with a cumulant expansion mode. When a sample solution is considered to be composed of two components of dispersed particles with small and large sizes, $g(\tau)$ is expressed as

$$g(\tau) = A_{\mathrm{Fast}} \exp(-\Gamma_{\mathrm{Fast}}\tau) + A_{\mathrm{Slow}} \exp(-\Gamma_{\mathrm{Slow}}\tau) , \tag{1}$$

where τ is the relaxation time, Γ_{Fast} and Γ_{Slow} are the relaxation rates, or inversed correlation times of fast and slow relaxation time components, and A_{Fast} and A_{Slow} are the constants indicating relative magnitudes of two components ($A_{\mathrm{Fast}} + A_{\mathrm{Slow}} = 1$). For the system showing polydispersity characteristics, analysis based on a cumulant expansion mode up to the second-order depending upon the deviations from a single exponential decay was employed [9]:

$$g(\tau) = \exp[-\Gamma_{\mathrm{Cumu}}\tau + (\mu_2/2!)\tau^2] , \tag{2}$$

where Γ_{Cumu} is the mean relaxation rate characterizing the weight averaged dispersed particles and $\mu_2/\Gamma^2_{\mathrm{Cumu}}$ is the dispersion index referring to the magnitude of deviation from the single exponential decay mode.

Hydrodynamic radius of the scattering particle, r_{H}, can be calculated from the estimated relaxation rate, Γ, with the Stokes–Einstein relation as

$$\Gamma = Dq^2, \qquad D = kT/6\pi\eta r_{\mathrm{H}} , \tag{3}$$

where Γ refers to Γ_{Fast}, Γ_{Slow}, or Γ_{Cumu}, D is the translational diffusion coefficient, q is the length of the scattering vector; $q = (4\pi n/\lambda)\sin(\theta/2)$ with n, λ, and θ being the refractive index of the medium, the wavelength of the incident beam, and the scattering angle, respectively, k is the Boltzmann constant, T is the absolute temperature, and η is the solvent viscosity. Hydrodynamic radii, r_{Fast} and r_{Slow}, were estimated from Eqs. (1) and (3) to discuss dispersion behavior of sodium oleate and oleic acid in NaCl aqueous solutions. On the other hand, in the system characterized with polydispersity, r_{Cumu} referring to a weight-averaged particle radius was estimated from Eqs. (2) and (3). In the present study, changes of the hydrodynamic radii, r_{Fast} and r_{Cumu}, as a size of the equivalent hydrodynamic sphere were examined as a function of the degree of ionization or pH. When the system was buffered by Tris, the estimated hydrodynamic radius was notified as $r_{\mathrm{Fast,Tris}}$ or $t_{\mathrm{Cumu,Tris}}$.

Results and discussion

Preliminary turbidity measurements

Figure 1 shows the typical absorbance at 350 nm, τ_{350}, vs. pH relationships at 25 °C measured for the sample solutions containing 10 mM oleic acid and 100 mM NaCl. The degree of ionization, α, vs. pH relationships were also presented in Fig. 1 to aid to recognize the pH conditions in the following experimental results as a function of the degree of ionization. Although the solution was clear at higher pH 9.8–10.5, where α is ranged from 1.0 to 0.95, the

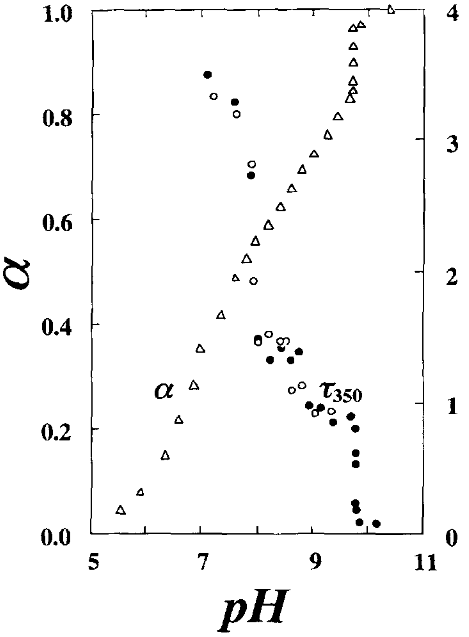

Fig. 1 A pH profile of turbidity formation at 350 nm wavelength τ_{350}, for the solutions containing 10 mM oleic acid and 100 mM NaCl. Turbidity formations were measured at time 0 (●) and 90 h (○) after the preparation of sample solutions. Note that the steady turbidity data are obtained immediately after the preparation of sample solutions. Relationships between the degree of ionization α, and pH (△) demonstrate the constant pH regions at 9.75

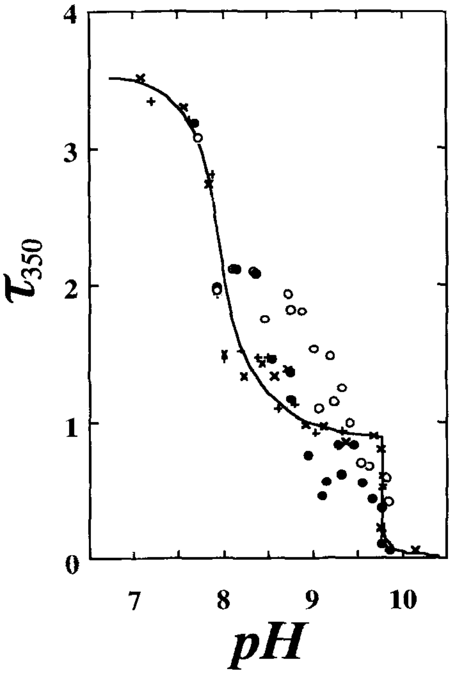

Fig. 2 A pH profile of turbidity formation at 350 nm wave length τ_{350} for the solutions containing 10 mM oleic acid and 100 mM NaCl with and without 20 mM Tris. Symbols (●) and (○) refer to Tris-containing solution, while (×), (+), and (solid line) refer to the Tris-free solution. Turbidity formations were measured at time 0 (●, ×) and 90 h (○, +) after the preparation of sample solutions

solution turbidity increased rapidly at pH around 9.7. Based on the reported H^+-ion titration experiments, the pH values of 10 mM oleic acid solution containing 100 mM NaCl stay at a constant level around pH 9.7 within a range of α from 0.95 to 0.80 [5]. This pH constant region was characterized as a three-phase equilibrium composed of sodium oleate micelles, acid–soap with R^-Na^+/RH ratio of 3, $(R^-Na^+)_3RH$, and the equilibrated solution. The present investigation aims mainly at clarifying the dispersion characteristics in these constant pH ranges, especially the formation and properties of micelles and sodium oleate/oleic acid–soap, by the dynamic light-scattering measurements. Further decreases in pH caused another steep increase in solution turbidity at around pH 8.0–8.5 as can be seen in Fig. 1. Similar turbidity increases at pH 8.6 were reported in 1 mM sodium oleate aqueous solution [4]. Then finally, separations of the oleic-acid oil droplets from aqueous phase at lower pH regions were observed even by eye.

Figure 2 demonstrates the comparison between pH changes in turbidity of the sample solutions containing 10 mM oleic acid and 100 mM NaCl with and without 20 mM Tris as a buffering agent. In the case without Tris, the turbidity–pH relationships were stable with time, whereas in the case of Tris buffering system, the solution turbidity increased during the long lasting times up to 90 h, especially at pH lower than 9. These results suggested that Tris molecules play some unknown role in aggregation processes of oleic acid. In the present study, possible involvements of Tris to the molecular aggregation processes in the system containing oleic acid, sodium oleate, and NaCl were also examined by the dynamic light-scattering measurements.

Effects of oleic acid and NaCl concentrations on the dynamic light-scattering characteristics: survey of the experimental conditions

To determine the appropriate experimental conditions of oleic acid and NaCl concentrations for the dynamic light-scattering measurements, hydrodynamic radius of scattering particles was estimated based on the cumulant expansion made analysis at the scattering angle of 90°. The effects of the oleic acid concentrations, 0.2–1.0 mM, were examined at pH 9.76 in the solutions containing 100 mM NaCl and 20 mM Tris. In these experimental conditions, the hydrodynamic radius of scattering particles in Tris

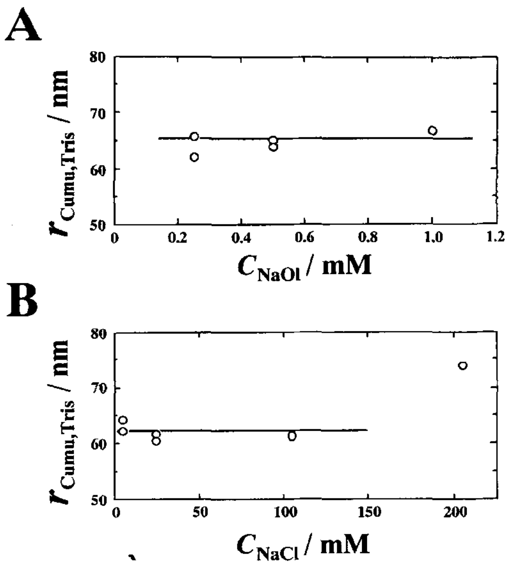

Fig. 3 (A) Effects of sodium oleate concentrations on hydrodynamic radius $r_{\mathrm{Cumu,Tris}}$, at pH 9.76 in solutions containing 100 mM NaCl and 20 mM Tris. (B) Effects of NaCl concentrations on hydrodynamic radius $r_{\mathrm{Cumu,Tris}}$, at pH 9.18 in solutions containing 0.5 mM sodium oleate and 10 mM Tris

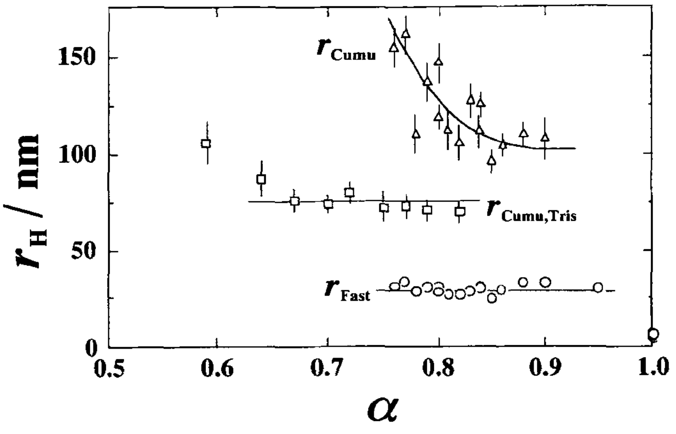

Fig. 4 Hydrodynamic radius as a function of the degree of ionization α. The values of r_{Fast} (○) and r_{Cumu} (△) were estimated for the solution containing 1 mM sodium oleate and 100 mM NaCl. The values of $r_{\mathrm{Cumu,Tris}}$ (□) were estimated for the solution containing 1 mM sodium oleate, 100 mM NaCl, and 10 mM Tris

containing media, $r_{\mathrm{Cumu,Tris}}$, amounted to around 65 nm, was not affected appreciably by sodium oleate concentration as shown in Fig. 3A. Figure 3B shows the effects of NaCl concentration on the hydrodynamic radius of scattering particle, $r_{\mathrm{Cumu,Tris}}$, in the sample solutions at pH 9.18 containing 0.5 mM sodium oleate and 10 mM Tris. Within the low NaCl concentration range studied, 5–105 mM, the $r_{\mathrm{Cumu,Tris}}$ values were suppressed to an almost constant level around 63 nm, whereas at the high NaCl concentration, 205 mM, the $r_{\mathrm{Cumu,Tris}}$ values significantly increased to around 74 nm probably due to the salting-out effect. Based on these preliminary measurements, the following dynamic light-scattering measurements were carried out mainly for the system containing 1 mM oleic acid and 100 mM NaCl.

Estimations of hydrodynamic radius of dispersed particle as a function of the degree of ionization

A series of the correlation functions, $g(\tau)$, were obtained at different degrees of ionization, α, for the system containing 1 mM oleic acid and 100 mM NaCl without Tris. The values of r_{Fast}, and r_{Slow} can be estimated from two negative slopes of the linear components satisfying the respective $\ln g(\tau)$ vs. $q^2\tau$ relationships. In the range of α, 0.7–0.9, a finely dispersed new phase, acid–soap, $(\mathrm{R^-Na^+})_3\mathrm{RH}$, contributed both to the light-scattering slow component and turbidity. The initial negative slopes of the $\ln g(\tau)$ vs. $q^2\tau$ relationships at $\tau = 0$ refer to the r_{Cumu} values. The results are presented in Fig. 4. In the system of $\alpha = 1$, where sodium oleate molecules are expected to form simple micelles, the estimated values of r_{Fast} ranged from 5.14 and 7.20 nm. These values seem to much larger than radius of the usual spherical micelle, so it was suggested that the association of sodium oleate micelles proceeds immediately after the micelle formation under these experimental conditions. The present 1 mM concentration of sodium oleate seems to be much higher than the first critical micelle concentration of sodium oleate, 0.2 mM, and another critical micelle concentration probably for the associated micelles with larger size was reported to be 0.7 mM [2]. Further inspections on the micelle formations of sodium oleate by the dynamic light-scattering measurements are described in the later section.

The r_{Fast} values, referring to the sizes of the major smallest scattering particles, stayed almost at a constant level around 30 nm in the wide range of the degree of ionization from 0.95 and 0.75. The size distribution of these particles was expected to be narrow, since the scattering angular dependence of the estimated radius values was relatively low. The particles with 30 nm radius appeared rapidly at α just below the unity and tend to disappear gradually below 0.85 as shown by the scattering intensity in Fig. 5. So it was suggested that sodium oleate micelles formed under fully ionized conditions readily associated to form aggregates with 5–7 nm radius and slight decreases in α or pH enhanced further association processes. Nearly constant amounts of the large associated micelles of sodium oleate with a radius of around 30 nm

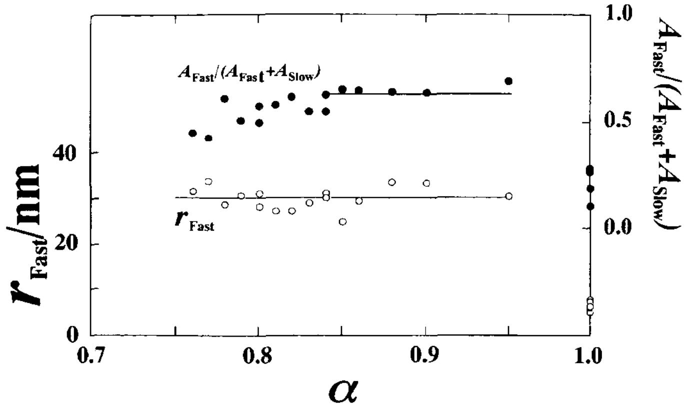

Fig. 5 Relative magnitude of the scattering intensity $A_{Fast}/(A_{Fast}+A_{Slow})$, (●) and hydrodynamic radius r_{Fast}, (○) of the fast scattering component as a function of the degree of ionization α. The double exponential decay mode analysis was applied to the solution containing 1 mM sodium oleate and 100 mM NaCl

exist at constant pH 9.7 within the range of α from 9.5 to 8.5. Rokhlenko et al. reported the easily associative characteristics of the oleate micelles based on the results that the scanning electron microscopic observations detected micelles with a diameter of 25 nm and that the spectrophotometric estimations for a micelle diameter presented the value of 120 nm [10]. It was suggested, based on these experimental results, that the first abrupt increases in turbidity at around pH 9.7 without Tris shown in Figs. 1 and 2 were caused from the formations of associated micelles with radius of 30 nm.

As can be seen in Fig. 4, the r_{Cumu} values, referring to the mean sizes of weight-averaged scattering particles, increase up to at least 150 nm below α of around 0.85 where the numbers of particle with 30 nm radius starts decreasing. Therefore, it was suggested that the second intensive increases in turbidity at α below 0.85, or at pH below 9, in Figs. 1 and 2 were caused by the increase in averaged particle sizes dispersed in the system. In the context of the second intensive turbidity increase, Drzymala has reported, based on the spectrophotometric measurements, that acidification of 1 mM sodium oleate aqueous solution creates, abruptly at pH 8.6, an oil phase in the form of droplets with a radius of 100–150 nm [4].

Under the three-phase equilibrium condition at constant pH around 9.7, associated micelles with radius of around 30 nm, acid–soap, $(R^-Na^+)_3RH$, and the equilibrated solution phase are coexisting. With the decreasing α, the acid–soaps were formed at the expense of the associated micelles. At the end of the three-phase equilibrium region, α of around 0.85, the associated micelles with 30 nm radius disappeared and, at the same moment, the weight averaged hydrodynamic radius, r_{Cumu}, was significantly increased. In these situations, polydispersity of scattering particles in the aqueous medium increased quickly. Accordingly, α of 0.7 or pH around 8.5 was the limit of the applicability of dynamic light-scattering measurements. Direct observations of the sample solutions by a laser confocal or phase-contrast microscope demonstrated the significantly wide distribution of the sizes of visible particles at low-pH regions in which the light-scattering and spectrophotometric measurements were not available.

Possible involvement of buffering agent, tris(hydroxymethyl)aminomethane, in molecular aggregation process

It has been generally recognized that tris(hydroxymethyl)-aminomethane (Tris) as a buffering agent also participates someway to the structural characteristics of molecules and molecular aggregates in solution. For instance, an ufasome (unsaturated fatty acid-some), lipsome-like vesicular assembly with a radius of around 1.5 μm, can be obtained only from the media containing Tris-buffer [11]. In this section, the effects of Tris on the micelle formation, association of micelle, and further higher-order aggregation processes of sodium oleate/oleic acid are examined. Figure 4 demonstrates that the hydrodynamic radius estimated based on the cumulant expansion mode analysis in Tris-containing media, $r_{Cumu,Tris}$, is smaller than that in Tris-free media, r_{Cumu}. These results are consistent with the turbidity measurement results in Fig. 2 showing that the turbidity value in Tris-containing media (open and filled circles) is somewhat lower than that in Tris-free media (solid line) in the pH ranges from 9.7 to 9.0. The constant values of $r_{Cumu,Tris}$ around 75 nm were observed over a wide range of pH or degree of ionization. So it was suggested that the increase in turbidity in Tris-containing media up to around pH 8 was mainly due to the increase in the number of particles with the hydrodynamic radius of around 75 nm. The increase in the particle size to around 100 nm seems to contribute also to the increase in turbidity above pH 8. On the contrary, in the Tris-free media, the turbidity increase at around pH 8 is suggested to be mainly due to the increase in particle size as discussed in the previous section.

The increase in the number of particles in Tris-containing media at pH around 8 was also inspected by a microscopic observation. None of the visible particles were detected in solution of pH around 10, however as the pH decreased, particles with a radius of less than 0.5 μm were increased and, at pH around 8, number of these particles increased sparklingly as a cause for the increase in turbidity. At pH around 7.5, solution became completely turbid and fibrous substances with 10–25 μm length, probably a crystalline phase consisting of oleic acid and sodium oleate, were observed. In the region of pH 8.0–7.5, large particles with a radius of 1.0–1.5 μm were simultaneously observed. The size and number of these particles were relatively insensitive to pH changes. There is a possibility that ufasomes or related aggregates are involved in the heterogeneous behavior of these solutions.

To examine the effects of Tris as a polyalcohol, 1,2-ethanediol and 1,2,3-propanetriol were substituted for Tris. Turbid solutions without Tris, such as sodium oleate-HCl, sodium oleate-HCl-1,2-ethanediol, and sodium oleate-HCl-1,2,3-propanetriol systems, caused the phase separation to form oil and aqueous layers. On the contrary, turbid solutions with Tris were stable to resist two-layered phase separation even after 1 month. Possible mechanisms to these Tris effects may arise from direct participation as a component to form mixed-micelles or other complexes. Further investigations are required to clarify the effects of Tris on the molecular aggregation processes including the formation of micelles, emulsions, and higher-ordered assemblies.

Further investigations on the micelle formation of sodium oleate

It is generally expected that sodium oleate forms simple spherical micelle under fully ionized conditions and that the radius of usual spherical micelle is ranged 2–3 nm. As mentioned earlier, the detected smallest value of the hydrodynamic radius estimated in the sample solution without Tris was around 5 nm which is somewhat larger than the radius of usual spherical micelle. To examine further on the micelle formation of sodium oleate, the effects of sodium oleate concentrations of the hydrodynamic radius were investigated. The estimated value of the hydrodynamic radius in these solutions with fully ionized conditions referred to the size of sodium oleate micelle. In the sample solutions without Tris, there existed some practical difficulties to keep the pH values of the fully ionized conditions during the filtration procedures and light-scattering measurements. The detected smallest value of the hydrodynamic radius was around 5 nm for the sample solutions containing 1 mM sodium oleate and 100 mM NaCl prepared with pH above 11. However, only slight decreases in the pH of sample solution caused rapid increases in radius of scattering particle to 7–16 nm, and in the sample solution prepared with pH at around 10, these values reached 20 nm. It was indicated that the sudden changes in the hydrodynamic radius are induced within the extremely narrow pH range.

The hydrodynamic radius of sodium oleate micelles were measured as a function of the sodium oleate concentration from 0.5 to 20 mM in the sample solutions prepared at pH 10.9. The values of micelle radius of 2–5 nm at 0.5 mM increased with increasing sodium oleate concentration and, above 10 mM, attained constant value around 12–14 nm. Sodium oleate as a surface active agent has been characterized by multiple critical micelle concentrations. Zimmels and Lin reported a series of the critical micelle concentrations, CMC I, II, and III as 0.2, 0.7, and 2.3 mM, respectively, based on the electrical conductivity and surface tension measurements at 26 °C [2]. It was reported that the increases in these critical micelle concentrations were less than 1%/°C up to 41 °C. The concentration ranges characterized by these stepwise micelle formation processes were reflected in the concentration-dependent increases of the hydrodynamic radius of scattering particles. As mentioned earlier, just a slight downward shift of pH from fully ionized conditions induces a significant increase in the associated micelle size and, finally, the pH-stable large associated micelles with a radius of 30 nm are appeared.

In the present study, the dispersion behavior of aqueous solution containing oleic acid, sodium oleate, and NaCl was examined by directly tracing the pH-dependent characteristics of dispersed particles using dynamic light-scattering technique. It was suggested that associated micelles and acid–soaps play dominant roles to decide dispersion behavior of the system. The complex and heterogeneous phase changes of the oleic acid containing system seem to relate someway to the homeostatic controls of biological systems and the stable operations of industrial mining processes.

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