A fluorescence probe study on effects of surfactants on cloud points in aqueous poly(*N*-isopropylacrylamide) solutions.

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ABSTRACT: Fluorescence probe methods were applied to investigate micelle formation of poly(*N*-isopropylacrylamide) (PNIPA) with two kinds of surfactants, anionic sodium *n*-dodecyl sulfate (SDS) or cationic *n*-dodecyltrimethylammonium chloride (DTAC), in aqueous solutions using pyrene or 1-pyrenecarboxaldehyde as fluorescence probes. Two PNIPA samples, one having a hydrophobic chain-end group and the other having a negatively-charged hydrophilic chain-end group, were used to investigate effects of the chain-end group on formation of the micelles. It was found that the critical aggregation concentration, at which the surfactant molecules start to bind to the PNIPA chains to form the micelles, is much lower for the PNIPA solutions containing SDS than for the solutions containing DTAC. This is consistent with the previous result that the cloud point in the PNIPA solutions containing SDS starts to increase from its value in the surfactant-free solutions at much lower concentration of added surfactant than that in the solutions containing DTAC. It was also found that there is a discrepancy in emission spectra for the solutions containing SDS between the two PNIPA samples but not for the solutions containing DTAC, indicating that the chain-end group of PNIPA may affect the microenvironmental polarity in the micelles composed of PNIPA and the surfactants.

KEY WORDS poly(*N*-isopropylacrylamide) / aqueous solution /
cloud point / surfactant / chain-end group /
fluorescence probe method / micelle formation /

RUNNING HEADS Effects of Surfactants in Aqueous PNIPA Solutions

Introduction

In recent years, we have made a series of experimental studies of phase behavior of aqueous poly(*N*-isopropylacrylamide) (PNIPA) solutions,[1–5] which we had conventionally considered to show lower-critical-solution-temperature (LCST) miscibility behavior near the human body temperature caused by breakdown of hydrogen bonds between polymers and surrounding water molecules. In the course of the studies,[1–5] we have found that the phase behavior is not as simple as usually considered and the behavior of their cloud-point curves is considerably affected by the kind of chain-end group of the PNIPA sample used and also by the degree of branching of the sample.

It is known that the phase behavior of aqueous PNIPA solutions is influenced also by an addition of surfactants.[6] Until now, not a few studies have been made of effects of surfactants on the phase behavior of aqueous PNIPA solutions.[7–15] In our previous paper,[16] we have reported results of the cloud points in aqueous PNIPA solutions with an addition of two kinds of surfactants, anionic sodium *n*-dodecyl sulfate (SDS) or cationic *n*-dodecyltrimethylammonium chloride (DTAC). In the study,[16] we used two low-molecular-weight PNIPA samples, one having a hydrophobic chain-end group (M sample) and the other having a hydrophilic negatively-charged chain-end group (R sample), to examine whether the chain-end group affects the behavior of the cloud points. Figure 1 reproduces the plots in ref 16 of the cloud point in the aqueous PNIPA solutions (polymer mass concentration $c_{\rm p} = 10$ mg ml^{-1}) with an addition of the two kinds of surfactants, SDS or DTAC, against the concentration $c_{\rm s}$ of the added surfactant. From the figure, it is found that the cloud points in the solutions of both the PNIPA samples with an addition of SDS increase monotonically and steeply with increasing $c_{\rm s}$. On the other hand, the cloud point in the solution of the M sample with an addition of DTAC is found to be constant for $c_{\rm s} \lesssim 27$ mM and then increase with increasing $c_{\rm s}$ for $c_{\rm s} \gtrsim 27$ mM. As for the solution of the R sample with DTAC, it is found that the cloud point first decreases with increasing $c_{\rm s}$, then passes through a minimum at $c_{\rm s} \simeq 11$ mM, and finally increases for $c_{\rm s} \gtrsim 11$ mM. The indication is that the behavior of the cloud point as a function of $c_{\rm s}$ depends on the kind of surfactants and also on the kind of chain-end group of PNIPA.

Figure 1

The above-mentioned increase in the cloud point in all the aqueous PNIPA solutions with an addition of the surfactants is considered to result from electrostatic repulsion between charged micells formed by binding of the surfactant molecules to the PNIPA chains through hydrophobic interations, as early suggested by Schild and Tirrell.[8] In the present study, we make a detailed examination of the micelle formation of PNIPA with the surfactant molecules by applying a fluorescence probe method. In this study, we use two kinds of fluorescence probe molecules, pyrene and 1-pyrenecarboxaldehyde, to examine the micelle formation comprehensively. As seen from Figure 1, the cloud point in the aqueous PNIPA solutions containing SDS starts to increase at much smaller c_s than that in the solutions containing DTAC, implying that SDS may bind to PNIPA to form micelles at much smaller c_s than DTAC. The first purpose of this study is to confirm this expectation. On the other hand, the decrease in the cloud point observed for the solution of the R sample containing DTAC for small c_s, as seen in Figure 1, is presumed to arise because the cationic DTAC molecule bound to the negatively-charged chain end of the R sample diminishes the hydrophilicity of its chain end. The investigation of the effects of the chain-end group on the binding of the surfactant molecules to the PNIPA chains is the second purpose of this paper.

EXPERIMENTAL PROCEDURE

Materials

The PNIPA sample M5 used in this study was a fraction newly separated by fractional precipitation from the original sample, which had been previously synthesized by radical polymerization in methanol using AIBN (azobisisobutyronitrile) as an initiator.[1] After the fractionation, the sample was purified and dried in the same way as that described in our previous paper.[1] We note that almost all of the initiating and terminating chain ends of the sample M5 are considered to be hydrophobic isobutyronitrile groups derived from AIBN.

The other PNIPA sample R5 was prepared by aqueous redox polymerization using a redox catalyst consisting of ammonium persulfate, $(NH_4)_2S_2O_8$ (Nacalai Tesque, Inc., Kyoto,

Japan), as the oxidative part, and sodium metabisulfite, $Na_2S_2O_5$ (Nacalai Tesque, Inc.), as the reductive part, following the procedure reported by Wooten *et al.*[17] The detailed procedure for the polymerization and purification of the sample was the same as that described in our previous paper,[5] except the present sample was not fractionated. We note that almost all of the initiating chain ends of the sample R5 are considered to be anionic sulfonate groups.[5] As for the terminating chain-end group of the sample R5, we do not have any detailed information. However, at least, it may be considered that the terminating chain-end group of the sample is not positively charged.

For the samples M5 and R5, the weight-average molecular weight M_w and the ratio of M_w to the number-average molecular weight M_n were determined from analytical gel permeation chromatography (GPC) with two serially connected columns, SB-805HQ and SB-804HQ (Showa Denko KK, Tokyo, Japan), connected to a solvent delivery pump L-7100 (Hitachi, Ltd, Tokyo, Japan) and a refractive index detector RI-930 (JASCO Corporation, Tokyo, Japan); *N*,*N*-dimethylformamide (DMF) containing 10 mM lithium bromide at 50 °C was used as an eluent, and twelve standard polystyrene samples (Tosoh Corporation, Tokyo, Japan, $M_w = 550 - 5.46 \times 10^6$) were used as reference standards. For the two samples, the values of M_w and M_w/M_n so determined are given in Table 1. We note that both the samples are atactic.[1,5] We also note that both the samples are considered to have small numbers of branch points.[1,5]

Table 1

The surfactants SDS (Wako Pure Chemical Industries, Ltd, Osaka, Japan) and DTAC (Tokyo Chemical Industry Co., Ltd, Tokyo, Japan) that were added into the aqueous PNIPA solutions in fluorescence measurements were of reagent grade. Pyrene (Nacalai Tesque, Inc.) and 1-pyrenecarboxaldehyde (Tokyo Chemical Industry Co., Ltd.) that were used as fluorescence probes were of reagent grade. Water used for the fluorescence measurements was highly purified through a water purification system Autopure WT101UV (Yamato Scientific Co., Ltd, Tokyo, Japan); its resistivity was 18.2 MΩ cm.

Fluorescence measurements

For the aqueous solutions of the PNIPA samples M5 and R5 with an addition of SDS or DTAC in which a small amount of pyrene or 1-pyrenecarboxaldehyde was solubilized as the fluorescence probe, steady-state fluorescence spectra were recorded on JASCO FP-6300 fluorescence spectrometer equipped with a peltier thermostatted single cell holder EHC-573 (JASCO Corporation). The solutions for the fluorescence measurements were prepared following a standard procedure reported in literatures[8,18] as follows: An aliquot of 10 μl acetone solution of pyrene or 1-pyrenecarboxaldehyde (1×10^{-3} M) was transfered into sample vials and then the acetone evaporated to dryness. Subsequently, a series of 10 ml aqueous PNIPA solutions containing SDS or DTAC was added into the vials under vigorous stirring so that a final pyrene or 1-pyrenecarboxaldehyde concentration might become *ca.* 1×10^{-6} M. The PNIPA concentration c_p was chosen to be 1.0 mg ml^{-1} in all the measurements, and the surfactant concentration was varied between 0 and 52 mM for SDS and between 0 and 53 mM for DTAC. Each solution was made homogeneous by continuous stirring at room temperature for 1 day.

Emission spectra of pyrene and 1-pyrenecarboxaldehyde in the aqueous solutions were measured with excitation at 337 nm and 365.5 nm, respsectively, at 25.0 °C. Slit widths were kept at 2.5 nm for pyrene and at 5 nm for 1-pyrenecarboxaldehyde during the measurements. For the solutions solubilizing pyrene, the ratio I_1/I_3 of the fluorescence intensities of the 0,0 band (373 nm) and the 0,2 band (383 nm) in the emission spectra was determined as a function of the surfactant concentration. As for the solutions solubilizing 1-pyrenecarboxaldehyde, the emission wavelength maximum λ_{max} in the emission spectra was determined as a function of the surfactant concentration. In addition, in order to examine temperature dependence of I_1/I_3 (of pyrene) and λ_{max} (of 1-pyrenecarboxaldehyde), the measurements were also made for the following aqueous solutions of the samples M5 and R5 at $c_p = 1.0$ mg ml^{-1}; the solutions without surfactant at various temperatures ranging from 26 °C to 37 °C, those with 0.35 mM SDS at various temperatures ranging from 26 °C to 38 °C, those with 3.5 mM SDS at various temperatures ranging from 26 °C to 60 °C, those with 11 mM DTAC at various temperatures

ranging from 26 °C to 36 °C, and those with 23 mM DTAC at various temperatures ranging from 26 °C to 39 °C.

RESULTS AND DISCUSSION

Emission spectra

Figure 2 shows examples of emission spectra of pyrene and 1-pyrenecarboxaldehyde solubilized in aqueous solutions of the sample M5 with additions of 0.35 mM SDS and 3.5 mM SDS at 25.0 °C, each at $c_{\rm p} = 1.0$ mg ml^{-1}. The solid and dashed curves represent the values of fluorescence intensities for pyrene and 1-pyrenecarboxaldehyde, respectively, at the indicated values of the concentration of SDS. The ratio I_1/I_3 of the first (373 nm) peak intensity to the third (383 nm) one of pyrene is 1.73 for the solution with 0.35 mM SDS, while it is 1.07 for the solution with 3.5 mM SDS. As well known, the ratio I_1/I_3 reflects microenvironmental polarity around the fluorescence probe pyrene, and it takes a high value when pyrene is located in polar media but it decreases as pyrene is solubilized in more hydrophobic (or nonpolar) environment of micelles that are formed in the solution.[8,19,20] The former value 1.73 of I_1/I_3 is very close to the value 1.74 obtained for the aqueous solution of the sample M5 without surfactant at the same $c_{\rm p}$ and at the same temperature, indicating that there exists practically no micelle in the solution with 0.35 mM SDS and the pyrene molecules are considered to be dispersed in the aqueous solution. The latter smaller value 1.07 of I_1/I_3 indicates that micelles are formed in the solution with 3.5 mM SDS, and most of pyrene molecules in the solution are incorporated into the micelles.

Figure 2

On the other hand, 1-pyrenecarboxaldehyde exhibits a blue shift in the emission spectra as the microenvironmental polarity around the probe molecule is decreased, and can be used as a fluorescence probe to investigate the formation of micelles.[8,21] In Figure 2, the values of $\lambda_{\rm max}$ of 1-pyrenecarboxaldehyde are 472 nm and 453 nm for the aqueous solutions of the sample M5 with 0.35 mM SDS and 3.5 mM SDS, respectively. We note that the value of $\lambda_{\rm max}$

for the aqueous solution of the sample M5 ($c_p = 1.0$ mg ml^{-1}) without surfactant at 25.0 °C is 472 nm, which is equal to the above value for the aqueous PNIPA solution with 0.35 mM SDS. As SDS concentration is increased to 3.5 mM, λ_{max} shifts to the lower wavelength 453 nm. These results are consistent with those obtained for the solutions solubilizing pyrene, *i.e.*, micelles are not formed in the solution with 0.35 mM SDS while a large number of micelles are formed in the solution with 3.5 mM SDS.

Surfactant concentration dependence

Aqueous PNIPA solutions containing SDS

In this subsection, we examine the behavior of I_1/I_3 of pyrene or λ_{max} of 1-pyrenecarboxaldehyde in aqueous PNIPA solutions, determined in the same manner as those mentioned in the last subsection, as a function of the concentration of the added surfactants. Figures 3a shows plots of I_1/I_3 of pyrene against the SDS concentration ([SDS]) for the aqueous solutions containing SDS at 25.0 °C. The unifilled circles represent the values for the aqueous solutions of the sample M5, and the unfilled triangles represent those for the aqueous solutions of the sample R5, both at $c_p = 1.0$ mg ml^{-1}. The filled diamonds represent the values for the aqueous SDS solutions without PNIPA. It is seen from the figure that I_1/I_3 for the aqueous solutions without PNIPA decreases gradually with increasing [SDS] and drops abruptly from *ca.* 1.7 to *ca.* 1.1 at [SDS] $\simeq$ 9 mM. This threshold value of [SDS] is regarded as the critical micelle concentration (CMC) of SDS, at which the SDS molecules start to form (homo)micelles. This value of CMC for SDS so estimated is in good agreement with literature values.[8,22] It is also seen from the figure that I_1/I_3 for the aqueous solutions of the PNIPA sample, either M5 or R5, containing SDS drops abruptly from *ca.* 1.7 at much lower [SDS] ($\simeq$ 0.9 mM) than that for the PNIPA-free solution. This result is considered to reflect the fact that the SDS molecules start to bind to the PNIPA chains to form complex micelles that are composed of PNIPA and SDS far below the CMC for SDS. The surfactant concentration at which the surfactant molecules and polymer chains start to form such complex micelles is called the critical aggregation concentration (CAC). The CAC for SDS in the PNIPA solutions is estimated to be *ca.* 0.9 mM, which is comparable to the values reported in literatures.[8,10]

Figure 3

Figure 3b shows plots of λ_{max} of 1-pyrenecarboxaldehyde against [SDS] for the aqueous solutions containing SDS at 25.0 °C. The symbols have the same meaning as those in Figure 3a. As in the case of I_1/I_3 shown in Figure 3a, λ_{max} for the aqueous PNIPA solutions starts to drop at about 10-times lower SDS concentration than that for the PNIPA-free solution, confirming the above conclusion that the CAC for SDS in the PNIPA solutions is much lower than the CMC for SDS.

Aqueous PNIPA solutions containing DTAC

Figures 4a shows plots of I_1/I_3 of pyrene against the DTAC concentration ([DTAC]) for the aqueous solutions containing DTAC at 25.0 °C. The unifilled circles represent the values for the aqueous solutions of the sample M5, and the unfilled triangles represent those for the aqueous solutions of the sample R5, both at $c_p = 1.0$ mg ml^{-1}. The filled diamonds represent the values for the aqueous DTAC solutions without PNIPA. As seen from the figure, I_1/I_3 for the aqueous DTAC solutions without PNIPA drops abruptly from *ca.* 1.7 to *ca.* 1.4 at [DTAC] $\simeq$ 20 mM. This value of [DTAC] is considered to be the CMC of DTAC, and it is in good agreement with a literature value.[22] I_1/I_3 for the aqueous solutions of the PNIPA sample, either M5 or R5, containing DTAC is seen to drop abruptly from *ca.* 1.7 at [DTAC]$\simeq$ 15 mM, which is slightly lower than the CMC for DTAC estimated above and is regarded as the CAC for DTAC in the PNIPA solutions.

Figure 4

Figure 4b shows plots of λ_{max} of 1-pyrenecarboxaldehyde against [DTAC] for the aqueous solutions containing DTAC at 25.0 °C. All the symbols have the same meaning as those in Figure 4a. The difference in the behavior of λ_{max} between the aqueous PNIPA solutions and the solution without PNIPA is almost the same as that in the behavior of I_1/I_3 shown in Figure 4a.

As seen from Figure 1, the cloud point in the aqueous PNIPA solutions containing SDS starts to increase from its value for the surfactant-free solutions at much lower c_s than that in

the aqueous PNIPA solutions containing DTAC. In either case, the increase in the cloud point is regarded as arising from the electrostatic repulsion between the charged micelles formed by binding of the surfactant molecules to the PNIPA chains. This electrostatic repulsion is considered to suppress the aggregation of the PNIPA chains, leading to the elevation of the cloud point. Since the above-estimated value of the CAC for SDS is much smaller than that of the CAC for DTAC, it may be considered that the negatively-charged micelles composed of PNIPA and SDS are formed at much lower c_s than the positively-charged micelles composed of PNIPA and DTAC. It may therefore be concluded that the difference in the value of c_s at which the cloud point in the aqueous PNIPA solutions with surfactant starts to increase between SDS and DTAC is caused by the difference in the value of CAC between the two kinds of surfactants.

Temperature dependence

Aqueous PNIPA solutions without surfactant

Next, we examine the temperature dependence of I_1/I_3 of pyrene and λ_{max} of 1-pyrenecarboxaldehyde solubilized in aqueous PNIPA solutions with and without surfactant. Figures 5a and b show plots of I_1/I_3 and λ_{max}, respectively, against temperature for the aqueous PNIPA solutions without surfactant. The unifilled circles represent the values for the aqueous solutions of the sample M5, and the unfilled triangles represent those for the aqueous solutions of the sample R5, both at $c_p = 1.0$ mg ml^{-1}. It is seen that I_1/I_3 for the aqueous solutions of the two PNIPA samples decreases gradually with increasing temperature and then drops steeply at threshold temperatures, which are estimated to be *ca.* 33.5 °C and *ca.* 35.0 °C for the samples M5 and R5, respectively. As for λ_{max}, it is seen that it keeps constant for lower temperature and then drops steeply at the same temperatures as in the cases of I_1/I_3. The steep drop in I_1/I_3 or λ_{max} is considered to reflect the fact that the PNIPA chains start to form aggregates at the threshold temperatures and subsequently the fluorescence probe molecules, which are dispersed in water for lower temperature, are incorporated into the aggregates above the threshold temperature. Thus, the temperature at which I_1/I_3 or λ_{max} drops steeply may be regarded as being approximately equivalent to the cloud point in the aqueous PNIPA so-

lutions. As pointed out in the previous paper,[5] the cloud point in the aqueous solution of the R sample determined from measurements of transmittance of light passing through the solution at a given c_p is *ca.* 1.5 °C higher than that of the M sample at the same c_p if the values of M_w for the two PNIPA samples are close to each other, because the hydrophilicity of the chain-end group is stronger for the R sample than for the M sample. The same tendency is seen in the "cloud point" determined above as the temperature at which the steep drop in I_1/I_3 or λ_{max} occurs. In addition, it is seen from Figure 5 that the value of I_1/I_3 or λ_{max} is slightly smaller for the sample M5 than for the sample R5 in the whole range of temperature examined, indicating that the microenvironment around the fluorescence probe molecules is more hydrophobic in the solution of the former sample than in the solution of the latter one. Consequently, it may be said that the chain-end group of the PNIPA chain may affect the microenvironmental polarity around the probe molecules in the aqueous PNIPA solutions without surfactant.

Figure 5

Aqueous PNIPA solutions containing SDS

Figure 6a shows plots of I_1/I_3 of pyrene against temperature for the aqueous PNIPA solutions containing SDS. The unfilled circles with pip up represent the values for the aqueous solution of the sample M5, and the unfilled triangles with pip up represent those for the solutions of the sample R5, both at [SDS]=0.35 mM. The unfilled circles with pip down represent the values for the aqueous solution of the sample M5, and the unfilled triangles with pip down represent those for the solution of the sample R5, both at [SDS]=3.5 mM. In all the solutions, c_p is 1.0 mg ml^{-1}. We note that 0.35 mM and 3.5 mM of the SDS concentration correspond to the values below and above the CAC for SDS, respectively, which is estimated at 25.0 °C in the last subsection. It is seen that I_1/I_3 for the aqueous solutions of the two PNIPA samples with 0.35 mM SDS exhibits almost the same behavior as that in the aqueous PNIPA solutions without surfactant shown in Figure 5a, *i.e.*, I_1/I_3 at [SDS]=0.35 mM decreases gradually with increasing temperature and then drops steeply at *ca.* 33.5 °C and *ca.* 35.0 °C

for the samples M5 and R5, respectively. On the other hand, I_1/I_3 for the aqueous solutions of the two PNIPA samples with 3.5 mM SDS decreases gradually with increasing temperature and then increases inversely at threshold temperatures, which are *ca.* 49 °C and *ca.* 51 °C for the samples M5 and R5, respectively. Since 3.5 mM of [SDS] is larger than the CAC for SDS, it may be considered that the SDS molecules form the complex micelles with the PNIPA chains and the pyrene molecules are incorporated in hydrophobic microenvironment of the micelles in the solutions. The increases in I_1/I_3 at [SDS]=3.5 mM, which start at *ca.* 49 °C and *ca.* 51 °C for the samples M5 and R5, respectively, may be considered to represent the fact that the pyrene molecules are transfered to more hydrophilic microenvironment as temperature is raised from these values. In this connection, we may conjecture that the complex micelles that are formed for lower temperature start to collapse at the threshold temperatures due to shrinking and/or aggregation of the PNIPA chains, and then the pyrene molecules are excluded from inside of the complex micelles, leading to the increase in I_1/I_3. Further, it is important to see that there is a discrepancy in the value of I_1/I_3 between the two PNIPA samples M5 and R5 at either value of [SDS]. This indicates that the chain-end group of PNIPA may affect the microenvironmental polarity around the pyrene molecules not only when the probe molecules are solubilized in the micelle-free PNIPA solutions containing SDS but also when they are incorporated in the PNIPA-SDS complex micelles.

Figure 6

Figure 6b shows plots of λ_{max} of 1-pyrenecarboxaldehyde against temperature for the aqueous PNIPA solutions containing SDS. The symbols have the same meaning as those in Figure 6a. The behavior of λ_{max} at [SDS]=0.35 mM for the aqueous solutions of the two PNIPA samples is similar to that of I_1/I_3 at the same value of [SDS] shown in Figure 6a, *i.e.*, λ_{max} drops steeply at *ca.* 33.5 °C and *ca.* 35.0 °C for the samples M5 and R5, respectively. However, λ_{max} at [SDS]=3.5 mM continues to increase gradually for both the PNIPA samples with increasing temperature in the whole range of temperature examined, in contrast to the case of I_1/I_3 at the same [SDS]. The difference in the behavior between I_1/I_3 and

λ_{max} at [SDS]=3.5 mM may possibly be regarded as arising from the difference in a manner of interactions of the fluorescence probe molecules with the complex micelles between the two kinds of fluorescence probes, because pyrene is a highly hydrophobic molecule while 1-pyrenecarboxaldehyde is a relatively polar molecule due to its formyl group. At either value of [SDS], there is seen to be a discrepancy in the value of λ_{max} between the two samples M5 and R5, confirmimg the above finding that the chain-end group of the PNIPA chain may affect the microenvironmental polarity around the fluorescence probe molecules not only in the micelle-free PNIPA solutions containing SDS but also in the complex micelles.

Aqueous PNIPA solutions containing DTAC

Figures 7a and b show plots of I_1/I_3 of pyrene and λ_{max} of 1-pyrenecarboxaldehyde, respectively, against temperature for the aqueous PNIPA solutions containing DTAC. The unfilled circles with pip up represent the values for the aqueous solution of the sample M5, and the unfilled triangles with pip up represent those for the solutions of the sample R5, both at [DTAC]=11 mM. The unfilled circles with pip down represent the values for the aqueous solution of the sample M5, and the unfilled triangles with pip down represent those for the solution of the sample R5, both at [DTAC]=23 mM. In all the solutions, c_p is 1.0 mg ml^{-1}. We note that 11 mM and 23 mM of the DTAC concentration correspond to the values below and above the CAC for DTAC, respectively, which is estimated at 25.0 °C in the last subsection. Therefore, it may be considered that the complex micelles between DTAC and PNIPA are formed in the solutions at [DTAC]=23 mM but not at [DTAC]=11 mM. It is seen that I_1/I_3 for the aqueous PNIPA solutions with 11 mM DTAC decreases gradually with increasing temperature and then drops steeply at *ca.* 34 °C, while that for the PNIPA solutions with 23 mM DTAC increases steeply at *ca.* 37 °C. As for λ_{max}, it is seen that the value for the aqueous PNIPA solutions with 11 mM DTAC drops steeply at *ca.* 34 °C, while that for the PNIPA solutions with 23 mM DTAC also drops steeply at *ca.* 37 °C in contrast to the case for I_1/I_3 for the same solution. It is more important to note that the values of I_1/I_3 or λ_{max} for the two PNIPA samples, M5 and R5, are in good agreement with each other at either value of [DTAC]. This agreement between the two PNIPA samples indicates that the difference in the

chain-end group of PNIPA does not cause the difference in the microenvironmental polarity around the probe molecules if DTAC (instaed of SDS) is added into the solutions. Considering the fact that the sample R5 has the anionic sulfonate group at its chain end, the cationic DTAC molecules are expected to be adsorbed selectively onto the negatively-charged chain end of the sample R5 and then the hydrophobic alkyl chains of DTAC around the chain end diminish its hydrophilicity, while this phenomenon does not occur for the sample M5 having the nonionic hydrophobic chain end. Consequently, the difference in the hydrophobicity of the chain end between the two PNIPA samples, M5 and R5, may be considered to virtually disappear in the solutions containing DTAC. As the result, the values of I_1/I_3 or $\lambda_{\max}$ for the solutions of the two samples agree well with each other, in the presence of DTAC, as observed in Figure 7.

Figure 7

Finally, we note that the decrease in the cloud point for the aqueous solutions of the R sample containing DTAC from its value for the surfactant-free solution, as seen in Figure 1 for lower c_s ($\lesssim$ 10 mM), may be considered to arise for the same reason as above, *i.e.*, the DTAC molecules selectively adsorbed onto the negatively-charged chain end of the R sample may diminish the hydrophilicity of its chain end.

CONCLUSION

We have determined I_1/I_3 of pyrene and $\lambda_{\max}$ of 1-pyrenecarboxaldehyde for the aqueous solutions of the two PNIPA samples, M5 having a hydrophobic chain-end group and R5 having a negatively-charged hydrophilic chain-end group, with the addition of two kinds of surfactants, anionic SDS or cationic DTAC. For all the solutions, I_1/I_3 or $\lambda_{\max}$ determined at 25.0 °C decreases abruptly at the CAC at which the surfactant molecules start to bind to the PNIPA chains to form the PNIPA-surfactant complex micelles. It has been found that the value of the CAC for SDS in the PNIPA solutions is much smaller than that for DTAC. The difference in the CAC between SDS and DTAC is considered to cause the difference in the

value of c_s at which the cloud point in the aqueous PNIPA solutions with surfactant starts to increase from its value for the surfactant-free solutions between the two kinds of surfactants.

For the aqueous solutions of the two PNIPA samples with 0.35 mM and 3.5 mM SDS and with 11 mM and 23 mM DTAC, I_1/I_3 and λ_{max} have been determined in the range of temperature from 25.0 °C to above the cloud points in the respective solutions. Since the values of CAC for SDS and DTAC in the aqueous PNIPA solutions have been found to be *ca.* 0.9 mM and *ca.* 15 mM, respectively, it may be considered that the PNIPA-surfactant complex micelles are formed in the solutions with 3.5 mM SDS and 23 mM DTAC but not in the solutions with 0.35 mM SDS and 11 mM DTAC. It has been found that I_1/I_3 or λ_{max} for the solutions containing SDS is smaller for the sample M5 than for the sample R5, in either case of 0.35 mM SDS or 3.5 mM SDS. This indicates that chain-end group of PNIPA may affect the microenvironmental polarity around the fluorescence probe molecules solubilized in the solutions containing SDS. On the other hand, the values of I_1/I_3 or λ_{max} for the solutions of the two PNIPA samples, M5 and R5, containing DTAC agree well with each other, in either case of 11 mM DTAC or 23 mM DTAC. The agreement of the value of I_1/I_3 or λ_{max} in the solutions containing DTAC between the two PNIPA samples is considered to arise because the cationic DTAC molecules are adsorbed selectively onto the negatively-charged chain end of the sample R5 and then the hydrophobic alkyl chains of DTAC around the chain end diminish its hydrophilicity, so that the difference in the hydrophobicity of the chain end between the two PNIPA samples virtually disappears in the solutions containing DTAC.

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Figure Captions

Figure 1. Plots of the cloud point in aqueous PNIPA solutions against the concentration c_s of the added surfactants: (○), the M sample with an addition of SDS; (●), the M sample with an addition of DTAC; (△), the R sample with an addition of SDS; (▲), the R sample with an addition of DTAC.[16] The values of the weight-average molecular weight M_w are 6.45×10^4 and 3.26×10^4 for the M and R samples, respectively. In all the solutions, the concentration c_p of the PNIPA samples is 10 mg ml^{-1}. The solid curves connect smoothly the respective data points.

Figure 2. Emission spectra of pyrene and 1-pyrenecarboxaldehyde solubilized in aqueous solutions of the sample M5 with additions of 0.35 mM SDS and 3.5 mM SDS at 25.0 °C and at $c_p = 1.0$ mg ml^{-1}. The solid and dashed curves represent the values of fluorescence intensities for pyrene and 1-pyrenecarboxaldehyde, respectively, at the indicated values of the concentration of SDS.

Figure 3. Plots of I_1/I_3 of pyrene (a) or λ_{max} of 1-pyrenecarboxaldehyde (b) in aqueous solutions of the sample M5 (○) and in those of the sample R5 (△), both containing SDS, and in aqueous SDS solutions without PNIPA (◆) against the concentration of SDS at 25.0 °C. In the PNIPA solutions, c_p is 1.0 mg ml^{-1}. The solid curves connect smoothly the respective data points.

Figure 4. Plots of I_1/I_3 of pyrene (a) or λ_{max} of 1-pyrenecarboxaldehyde (b) in aqueous solutions of the sample M5 (○) and in those of the sample R5 (△), both containing DTAC, and in aqueous DTAC solutions without PNIPA (◆) against the concentration of DTAC at 25.0 °C. In the PNIPA solutions, c_p is 1.0 mg ml^{-1}. The solid curves connect smoothly the respective data points.

Figure 5. Plots of I_1/I_3 of pyrene (a) or λ_{max} of 1-pyrenecarboxaldehyde (b) in aqueous PNIPA solutions without surfactant against temperature: (○), the sample M5; (△), the sample R5. In both the solutions, c_p is 1.0 mg ml^{-1}. The solid curves connect smoothly the respective data points.

Figure 6. Plots of I_1/I_3 of pyrene (a) or λ_{max} of 1-pyrenecarboxaldehyde (b) in aqueous

PNIPA solutions with an addition of SDS against temperature: (○ with pip up), the sample M5 at [SDS]=0.35 mM; (△ with pip up), the sample R5 at [SDS]=0.35 mM; (○ with pip down), the sample M5 at [SDS]=3.5 mM; (△ with pip down), the sample R5 at [SDS]=3.5 mM. In all the solutions, $c_{\rm p}$ is 1.0 mg ml^{-1}. The solid curves connect smoothly the respective data points.

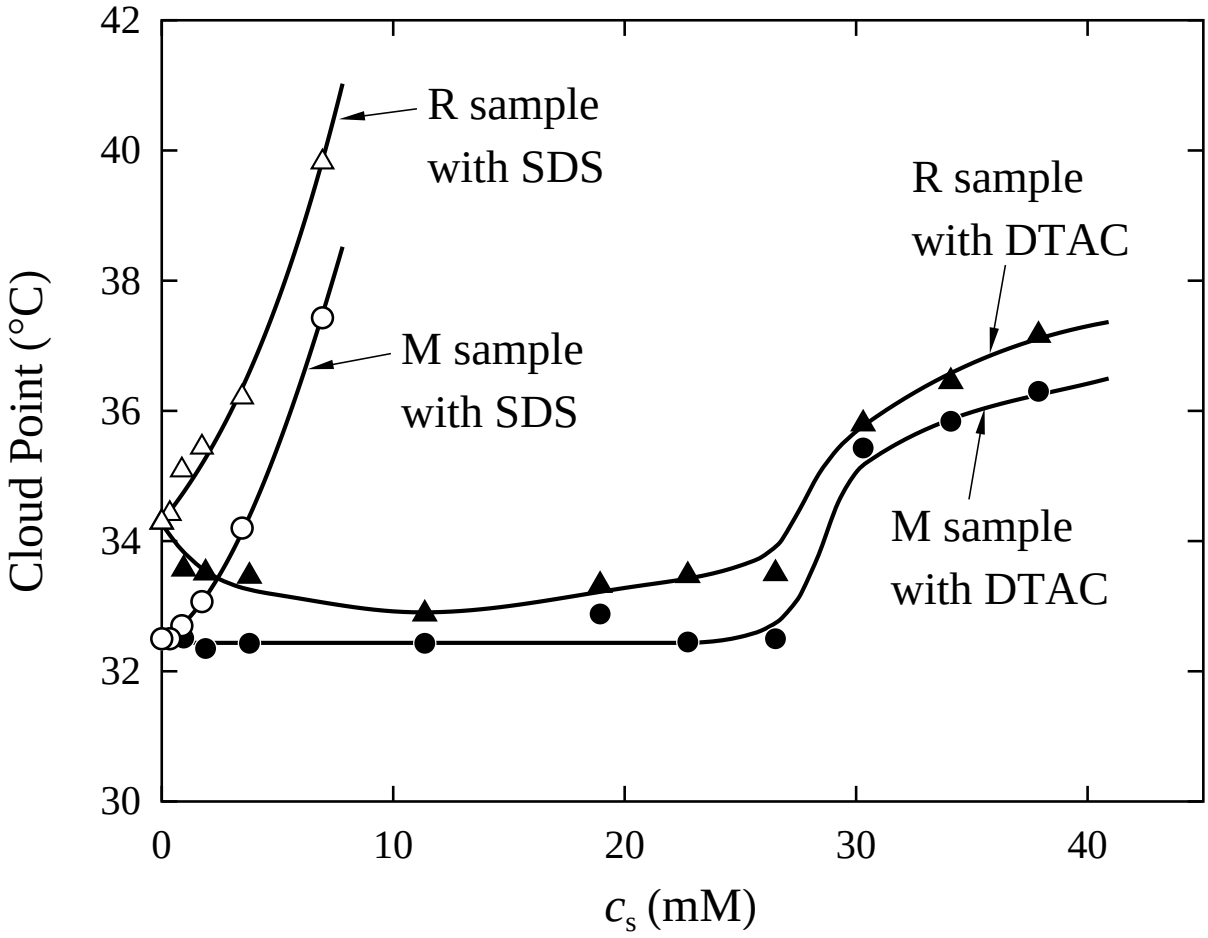
Figure 7. Plots of I_1/I_3 of pyrene (a) or $\lambda_{\rm max}$ of 1-pyrenecarboxaldehyde (b) in aqueous PNIPA solutions with an addition of DTAC against temperature: (○ with pip up), the sample M5 at [DTAC]=11 mM; (△ with pip up), the sample R5 at [DTAC]=11 mM; (○ with pip down), the sample M5 at [DTAC]=23 mM; (△ with pip down), the sample R5 at [DTAC]=23 mM. In all the solutions, $c_{\rm p}$ is 1.0 mg ml^{-1}. The solid curves connect smoothly the respective data points.

Table Caption

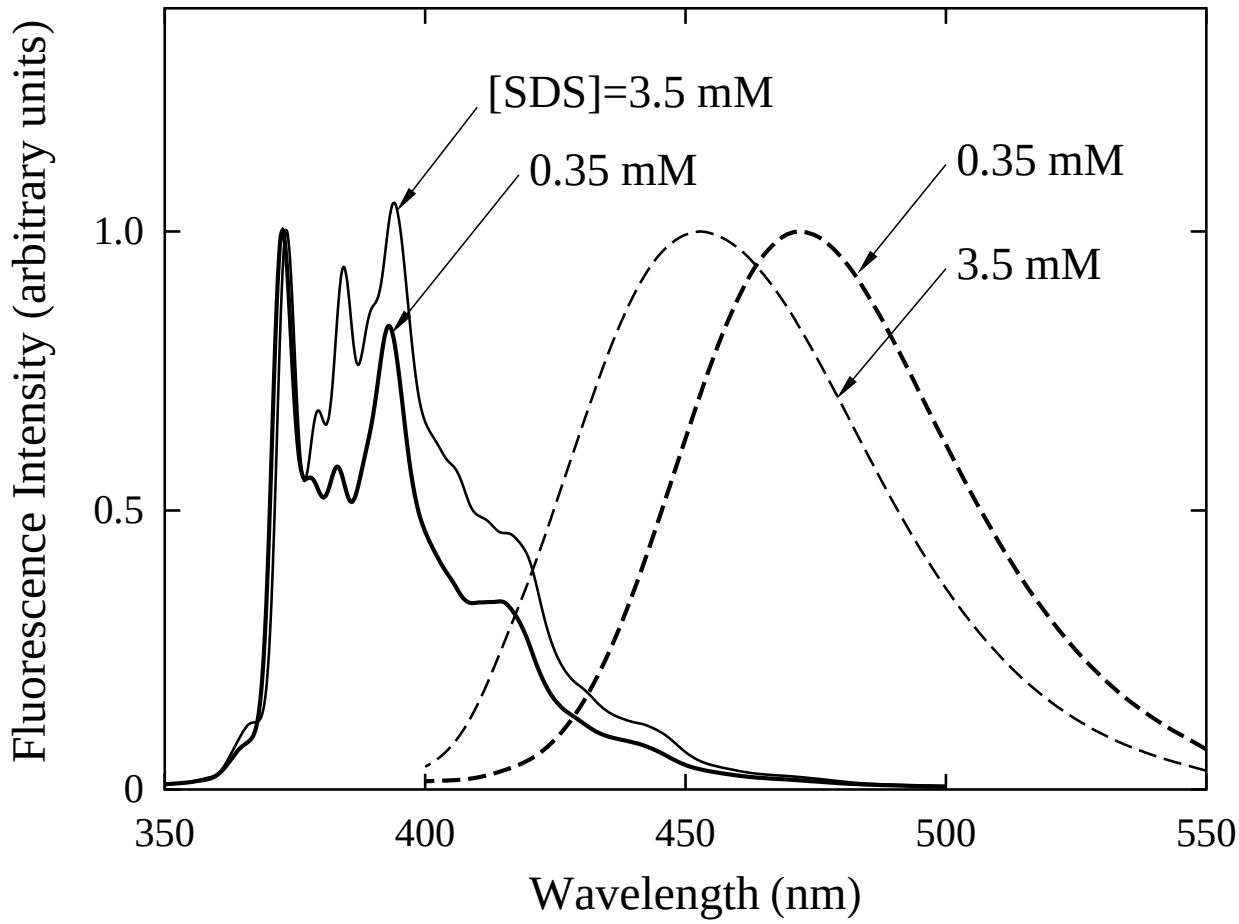
Table 1. Values of M_{w} and $M_{\mathrm{w}}/M_{\mathrm{n}}$ for Poly(N-isopropylacrylamide)

Table 1. Values of M_{w} and $M_{\mathrm{w}}/M_{\mathrm{n}}$ for Poly(*N*-isopropylacrylamide)

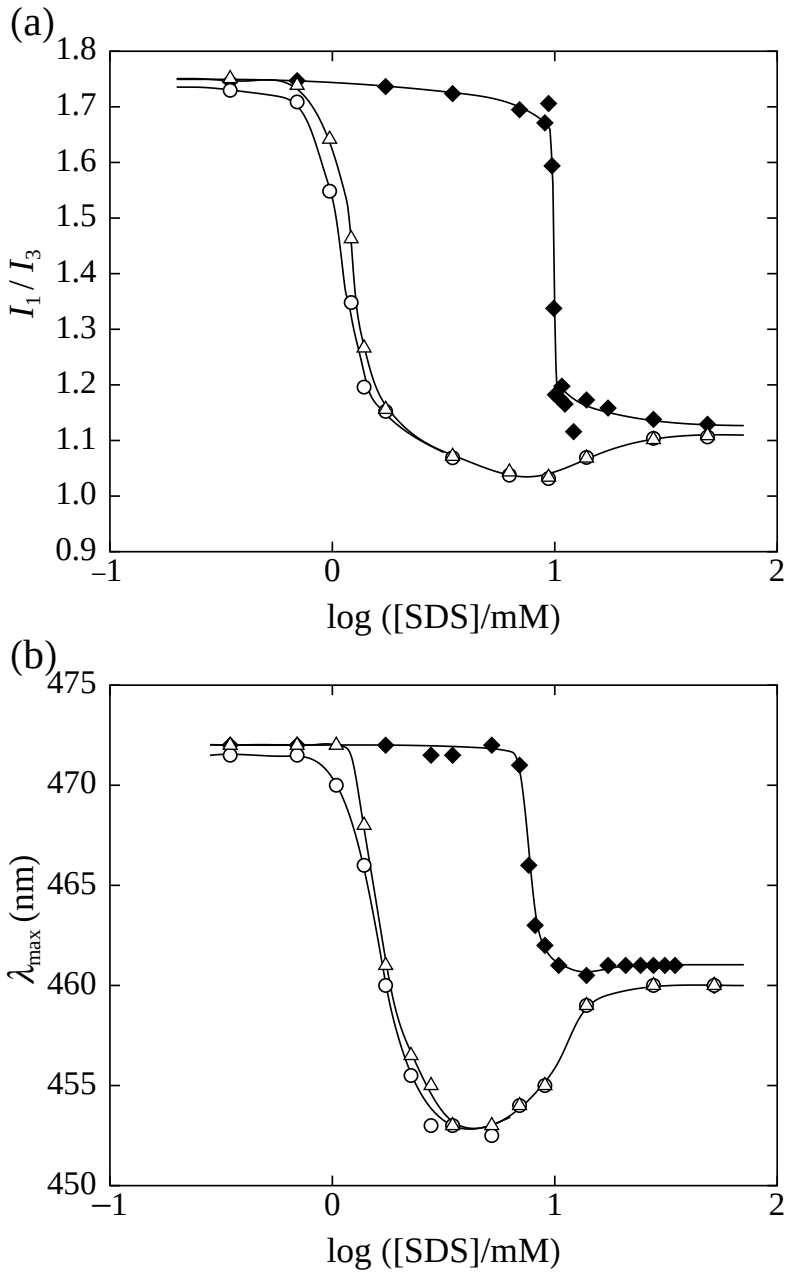
sample	M_{w}	$M_{\mathrm{w}}/M_{\mathrm{n}}$
M5	5.16×10^4	1.10
R5	5.80×10^4	1.51



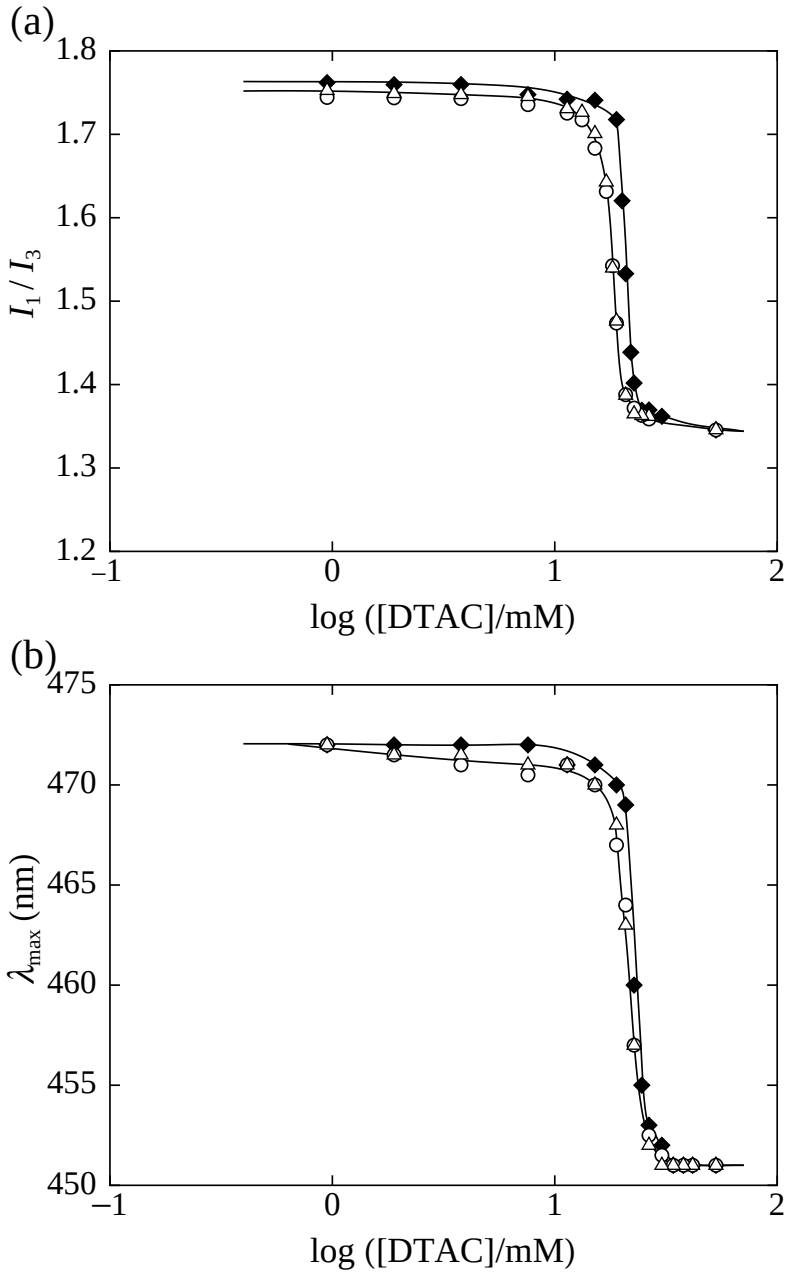
M. Osa *et al.*, Figure 1



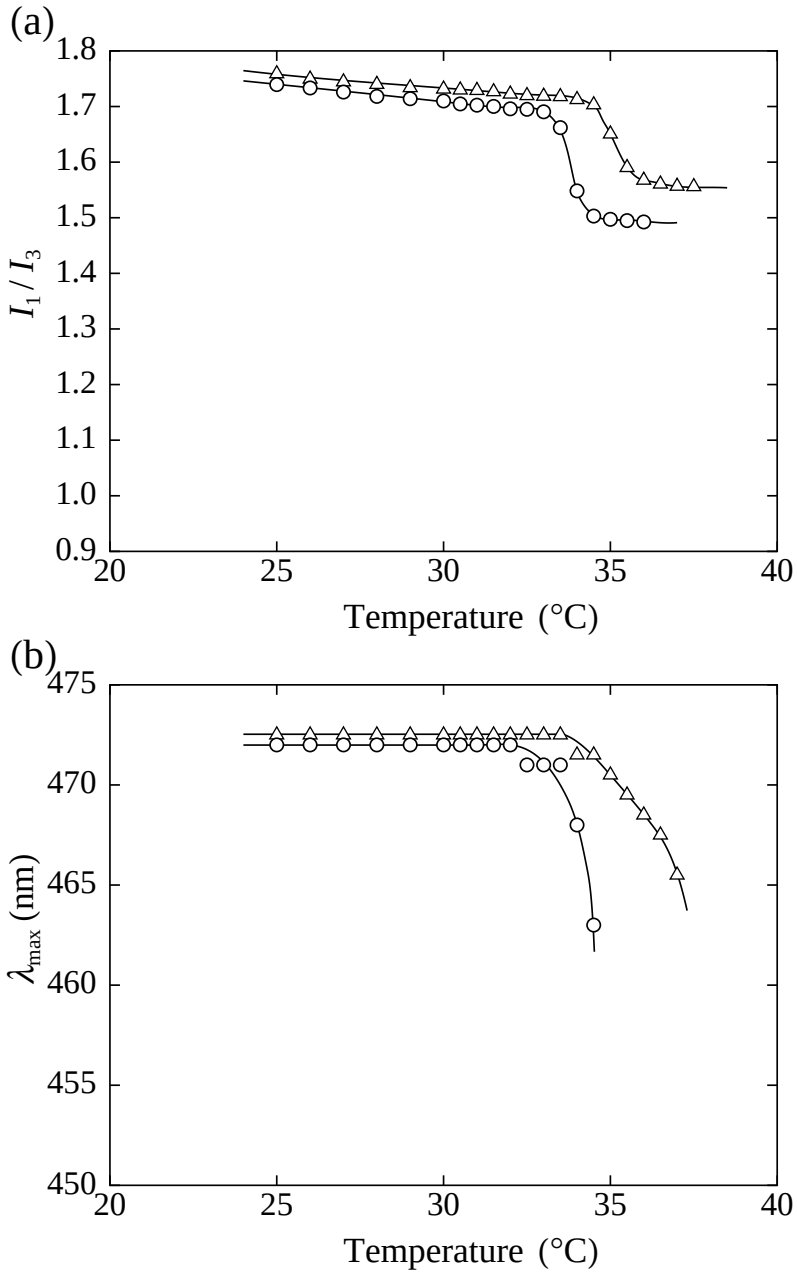
M. Osa *et al.*, Figure 2



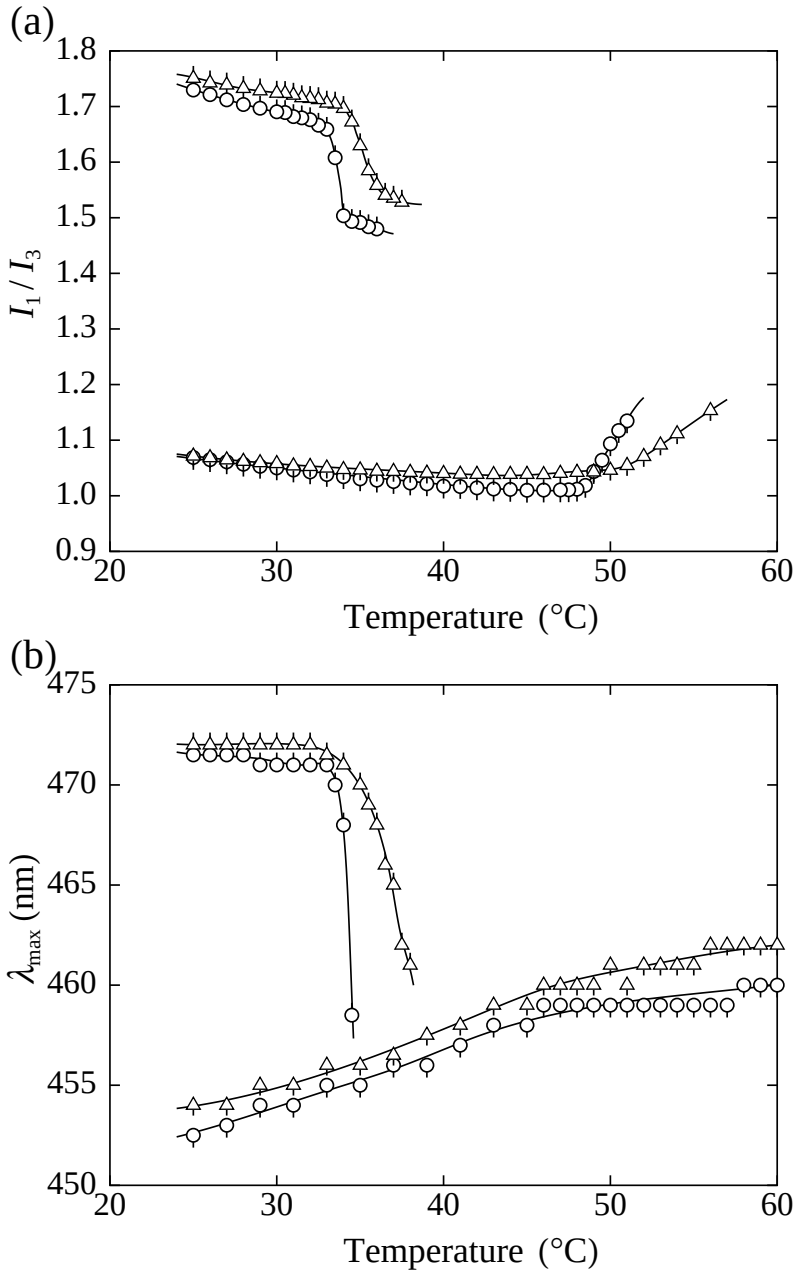
M. Osa *et al.*, Figure 3



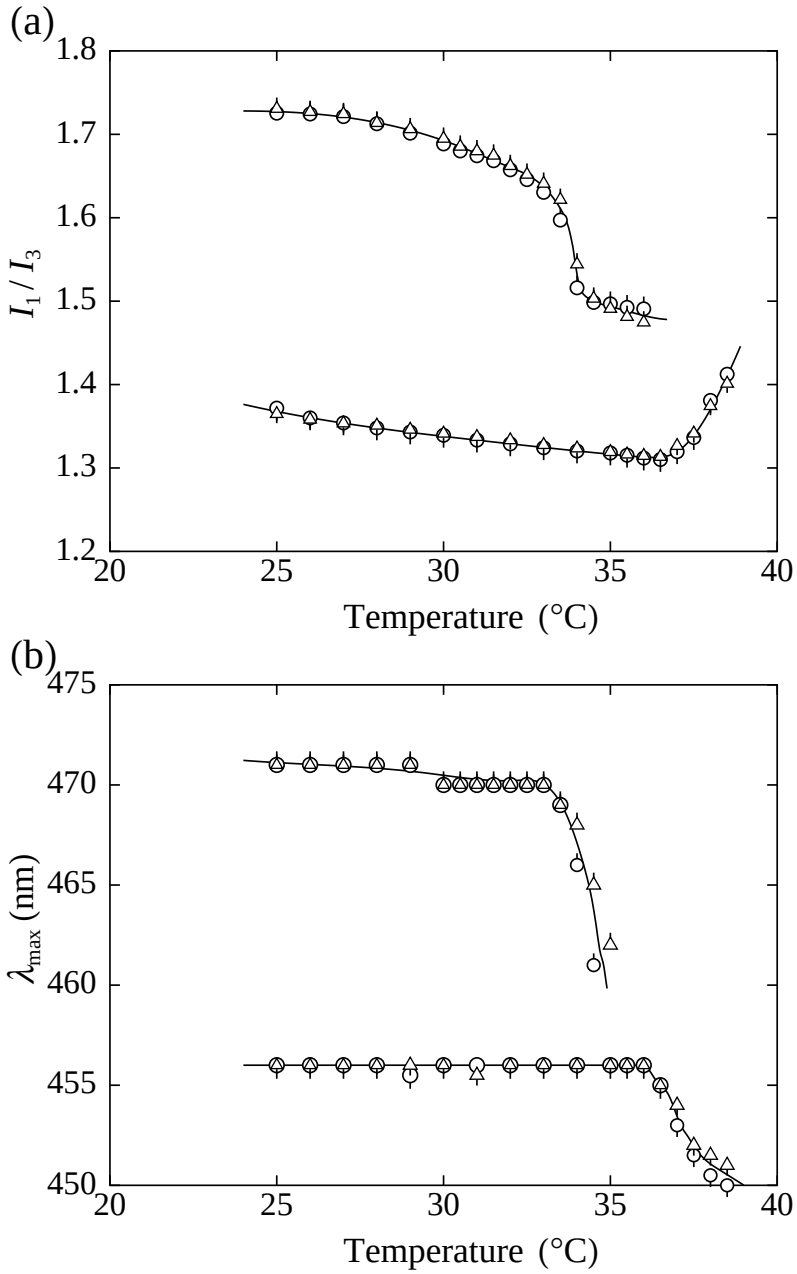
M. Osa *et al.*, Figure 4



M. Osa *et al.*, Figure 5



M. Osa *et al.*, Figure 6



M. Osa *et al.*, Figure 7

Graphical Abstract:

Fluorescence probe methods were applied to investigate micelle formation of poly(N-isopropylacrylamide) (PNIPA) with surfactant, sodium n-dodecyl sulfate (SDS) or n-dodecyltrimethylammonium chloride (DTAC), in aqueous solutions. Two PNIPA samples, one having a hydrophobic chain-end group (M sample) and the other having a negatively-charged hydrophilic chain-end group (R sample), were used to investigate effects of the chain-end group on the micelle formation. It is found that the microenvironmental polarity in the formed micelles depends on the kinds of chain-end group and surfactant.