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Microviscosity in AOT Reversed Micellar Core Determined with a Viscosity-sensitive Fluorescence Probe

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Microviscosity in AOT reversed micellar core, η, was determined with a viscosity-sensitive fluorescent probe, auramine O (AuO), as a function of R (=$[H_2O]/[AOT]$). With the increase in R, The η decreased rapidly in the region of $R<10$, and leveled at about R=20. AuO molecules located in the vicinity of water/surfactant interface suggested the presence of water bound to polar heads of AOT.

It is widely known that sodium bis (2-ethylhexyl) sulfosuccinate (Aerosol-OT or AOT) forms reversed micelle in various hydrophobic organic solvents and solubilizes relatively large amount of water in the interior core (water pool). Such core can provide a polar reaction field. Microviscosity in the interior core, as well as polarity, is important factor to use as a polar reaction field.

Steady-state[1-4] and transient[5-7] fluorescence depolarization techniques have been used to estimate the η in AOT reversed micellar core. However in the depolarization method, it is necessary to separate the effect of rotational motion of micelle itself from that of probe in micellar core, and to assume the mode of rotational motion of probe. This paper describes the η determined by the unpolarized steady-state fluorescence spectroscopy with a fluorescent probe, auramine O (AuO), of which the fluorescence quantum yield (Φ_f) increases with the increase in viscosity of media regardless of the solvent polarity.[8]

The Φ_f of AuO correlates with quenching phenomenon induced by internal rotation of dimethylaniline groups, and the internal rotation is affected by solvent viscosity.[8] The relationship between the Φ_f of AuO in glycerol-water mixtures or pure water and the η was examined in

advance. The η of glycerol-water mixtures was determined from the density of the mixtures measured with a pycnometer at 25 ± 0.3 °C. The AOT reversed micelle solution including AuO was prepared by solubilizing AuO aqueous solution ([AuO]=10^{-2}M (1 M = 1 mol dm^{-1})) in AOT cyclohexane solution ([AOT]=10^{-2}M) and the absorbance at 430nm of the micelle solution including AuO was maintained within the range of 0.13-0.18. The probe is insoluble in cyclohexane. The chemical structures of AuO and AOT, and the absorption and fluorescence spectra of AuO in glycerol are shown in Figs.1 and 2, respectively.

Figure 3 shows the relation of Φ_f^{-1} with $T\eta^{-1}$ (T: absolute temperature) in wide viscosity range. The values of Φ_f^{-1} coincide well with the data of Oster et al.,[8] although their data were measured in very narrow range of $T\eta^{-1}$.

Since cationic AuO seems to be located in the vicinity of anionic heads in AOT reversed micelles, the present method provides the η of around oil/water interface. Figure 4 shows the η determined from the working curve in Fig.3 as a function of R (=[H_2O]/[AOT]). As R value increases, the η rapidly decreased below R=10 and then leveled, and finally the solutions became turbid above R=28 owing to the limit of the solubilizing power for water. The higher viscosities in the small R region may be due to both effects of the increase in microviscosity in the water pool due to restriction by polar heads of AOT and restriction of AuO molecule itself by them. It is to note that the η at fully expanded state (ca. 18 cP)(1 P = 0.1 Pas) are considerably larger than that of ordinary bulk water at 25 °C (ca. 1 cP). Keh et al.[2] reported using an anionic dye (3,4,9,10-perylene sodium tetracarboxylate) which presents

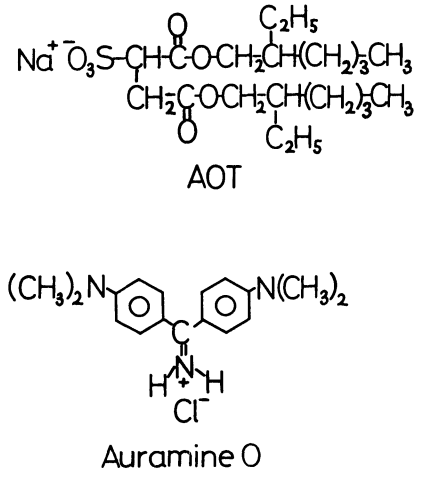

Fig. 1. Chemical structures of probe and surfactant used.

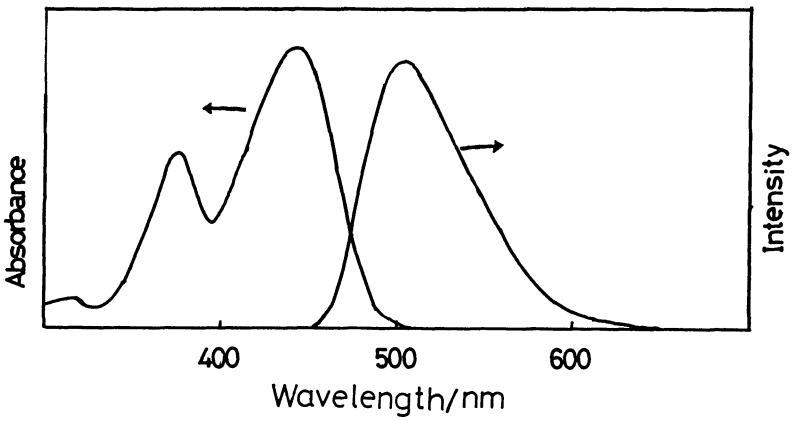

Fig. 2. Absorption and fluorescence spectra of AuO in glycerol.

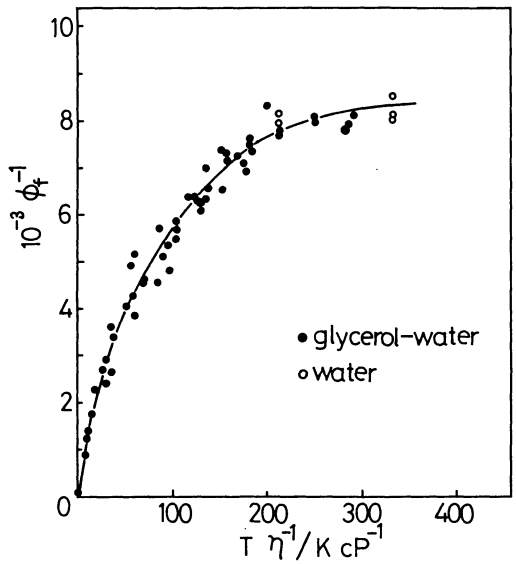

Fig. 3. The relationship between the fluorescence quantum yield of AuO and viscosity of media.

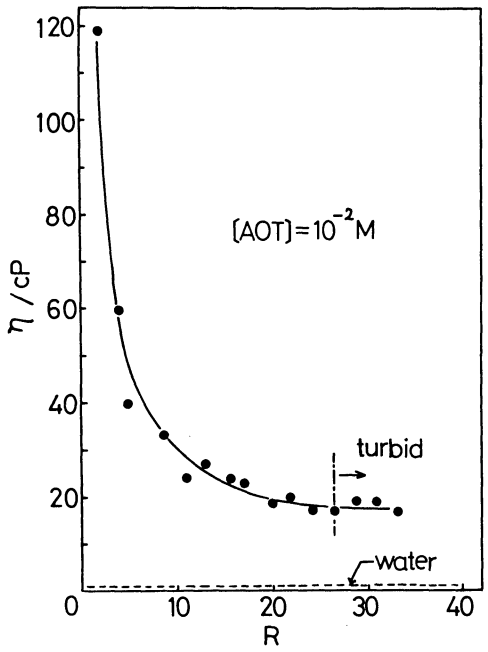

Fig. 4. Microviscosity in AOT reversed micellar core as a function of R.

around the center of the water pool owing to electrostatic repulsion that the water not bound to the polar heads become available as AOT micelle expands. The connection with our results suggests heterogeneous structure consisting of bound and not bound water. This conclusion coincides satisfactorily with a "biphase" model for water pool in AOT reversed micelle presented by Kondo et al.[3] and Zinsli[6] from the fluorescence depolarization results.

The concentration quenching of AuO fluorescence can be neglected because each micelle includes one probe or does not at all statistically. Furthermore Φ_f of AuO both in aqueous and glycerol solution remained constant by the addition of sodium ethansulfonate in the range of 10^{-4} to 10^{-1} M, indicating that the quenching due to polar heads of AOT does not occur in fact.

Since to our knowledge there is no work in which the microviscosity around water/surfactant interface was quantitatively measured using cationic dye, the absolute values of the microviscosity in the present study can not be directly compared with other data. Zinsli[6] estimated by computer simulation of the time-dependent fluorescence and polarization data the microviscosity in viscous polar boundary layer in AOT reversed micellar core on the basis of a model in which the excited probe molecules moves in the core consisting of viscous and fluid phases and are quenched at water/surfactant interface. The calculated values of the microviscosity are 85 ± 15 cP at R=5.5, 24 ± 4 cP at R=9.2, 16 ± 4 cP at

R=11.1, and 8 ± 3 cP at R=18.5. These values are roughly consistent with our data in the region of R<10, but are lower than our data in R>10.

The AuO method does not need to assume structural and phenomenal model, and are very simple technique by means of unpolarized steady-state fluorescence spectroscopy. Thus the use of viscosity-sensitive and site-selective AuO probe makes possible rapid determination of the microviscosity in water pool of reversed micelles.

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