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Dynamic and spectroscopic studies of nano-micelles comprising dye in water/ dioctyl sodium sulfosuccinate /decane droplet microemulsion at constant water content

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ABSTRACT

In the present work, the dynamic and spectroscopic properties of water-in-decane dioctyl sodium sulfosuccinate (AOT) microemulsions comprising dye, Rhodamine B (RB), were studied by varying content of decane at the constant water content (W = 20), by using dynamic light scattering (DLS), UV/visible, and fluorescence techniques. The characterization results of DLS of AOT micelles showed that by decreasing concentration of Rhodamine B in the water/AOT/decane microemulsion, the inter-droplet interactions changed from attractive to repulsive as the mass fraction of nano-droplets (MFD) increased. A deviation in the absorption spectra of Rhodamine B from the Beer's law at the high Rhodamine B concentration (0.001) was observed in the AOT reversed micelles. The Quenching in the emission intensity of AOT droplets comprising Rhodamine B and red shift in λ_{max} of fluorescence of dye was observed as a function of concentration of RB in AOT RMs. The Stokes shift of AOT droplets containing the high concentration of RB, increased with mass fraction of nano-droplet (MFD), whereas at the low Rhodamine B concentration, its variation remained constant up to MFD = 0.07, and then increased.

1. Introduction

In core-shell structure of AOT reversed micelles (RMs), the AOT-coated water nano-droplets are formed and dispersed in a bulk solvent of oil. In the AOT reversed micelles that are optically transparent, the hydrophilic head groups of AOT surfactant are embedded in the polar dispersed phase (water droplet) and its hydrophobic tails are directed towards the continuous organic phase [1–6].

The nanometer-sized water droplets are formed based on specific ratios of the water, surfactant, and organic solvent in the RMs. The structure, size, and property of water nano-droplets in the RMs are affected by the water-to-surfactant molar ratio, popularly is showed as the W value, W = [water or polar solvent]/[Surfactant]) [1–6] and the droplet-to-total components mass ratio, generally is represented as the mass fraction of nano-droplet (MFD) value, MFD = $M_{nano\text{-}droplet}/M_{total}$[7].

The water molecules in nanometer sized-length scales and at interfaces play a key role in many biological and physicochemical processes. The water molecules in confined nano-dimension locations and near interfaces induce the different dynamics in liquids than their bulk counterparts owing to surface-to-volume effect [8–10]. On the other hand, the AOT RMs generate polar/non-polar interfaces and nanometer-sized locations for the water-soluble additives such as fluorescent dyes. In addition, the water-in-oil droplet microemulsions influence the photo-physical properties of hydrophilic probes different from their bulk counterparts [7,10].

It is important to note that Rhodamine B (Fig. 1s) is a hydrophilic dye, which is widely used as fluorescent dye to characterize the polymer nanoparticles surface, bilayer and lipid membranes fluidity etc [11,12].

In previous studies, the AOT RMs containing the different hydrophilic fluorescent dyes, at the different water content (the different W value) have been investigated [13–20]. Previously, also, the aqueous solution of the cationic dye of Rhodamine B has been studied, but not in the water/AOT/decane system based on the Rhodamine B different concentrations at the constant water -to-AOT molar ratio (W = 20) and various contents of oil, to our

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knowledge [31–33]. Therefore, in the present research, the photophysics of water nano-droplets containing the different RB concentrations was studied at the constant water content (W = 20) within the water/AOT/decane inverse microemulsion by changing oil content of decane by the DLS, UV–visible, and Fluorescence techniques.

2. Experimental

2.1. Materials

The dioctyl sodium sulfosuccinate, AOT (Sigma–Aldrich,Germany, purity >99%), decane (Sigma–Aldrich,Germany, purity >99%) and cationic dye, Rhodamine B (Sigma–Aldrich,Germany, purity >99%)) with fluorometric grade were used as received.

2.2. Preparation of AOT nano-droplets comprising Rhodamine B

The nanometer-sized AOT droplets containing different Rhodamine B concentrations were prepared by mixing the certain mass values of AOT, decane and water containing different RB concentration based on the water-to-surfactant molar ratio of W = 20, and finally, the prepared stock solution of AOT RM was diluted with the decane oil based on the certain mass fraction of nano-droplet (as a function of MFD) at room temperature (RT). The mass ratio of Rhodamine B-to- water, $Y = m_{RB}/m_{water}$, was defined as concentration of the Rhodamine B in the AOT RMs[7].

2.3. Characterization of AOT nano-droplets

To obtain the autocorrelation function and size distribution of AOT RMs was used from dynamic light scattering (DLS) technique using a Zetasizer Nano ZS (Malvern Instruments, Germany) equipped with a He–Ne laser source (633 nm) with vertically polarized light.

The UV/vis absorption spectra of the AOT RMs was carried out by using a UV-1650 PC spectrometer (Shimadzu) in the wavelength of 300–700 nm. The emission spectrum of samples at the excitation wavelength of 554 nm was recorded with a JASCO FP-6200 spectrofluorimeter. The absorbance and fluorescence of the AOT RM samples was measured using a quartz cuvette.

3. Result and discussion

3.1. Theory of dynamic light scattering

Dynamic light scattering (DLS) is a great tool to characterize the size and diffusion coefficient of particles in a colloidal solution. The time-dependent scattered light intensity from a colloidal solution is a fluctuating quantity that depends on the size, Brownian motion and diffusive behavior of particles in solution and viscosity of continuous phase. These fluctuations can be analyzed in terms of the normalized autocorrelation function, $g1(\tau)$, of the scattered electrical field for a given delay time τ, which contains information about the structure and the dynamics of the scattering particles [21,22].

$$g^1(q,\tau) = \frac{\langle E(q,t)E^*(q,t+\tau)\rangle}{\langle I(q,t)\rangle} \quad (1)$$

where, E^* is the complex conjugated of E. Experimentally, the intensity correlation function, $g^2(q, \tau)$, is determined as following [21,22]:

$$g^2(q,\tau) = \frac{\langle E(q,t)E^*(q,t)E(q,t+\tau)E^*(q,t+\tau)\rangle}{\langle I^2(q,t)\rangle} \quad (2)$$

The normalized autocorrelation function, $g^2(q,\tau)$, is converted to the autocorrelation function of the scattered light electric field, g1 (q, τ) by the Siegert relationship [21,22].

$$g^2(q,\tau) = 1 + |A\exp(-\Gamma\tau)|^2 \quad (3)$$

Here, A is an instrumental constant. For a colloidal solution containing mono-disperse particles, the function of $g^1(q,\tau)$ is represented by a single exponential decay curve [21,22,25]:

$$g^1(q,\tau) = A\exp(-\Gamma\tau) \quad (4)$$

The decay rate, Γ, is converted to the diffusion coefficient using [21,22,25]:

$$D = \Gamma/q2 \quad (5)$$

Where q is the scattering vector [59–63]. Finally, the collective diffusion coefficient of water nano-droplets can be interpreted as the hydrodynamic radius following the Stokes-Einstein relation [21,22,25]:

$$r_h = \frac{K_B T}{6\eta\pi D} \quad (6)$$

Where k is Boltzmann's constant, T is the temperature in K, and η is the viscosity of solvent.

The rotational correlation time (τ_r) of spherical droplets containing fluorescent dye in the AOT RM was obtained by following the Stokes-Einstein-Debye (SED) hydrodynamic model [21,22,25].

$$\tau_r = \frac{4\pi\eta r_h^3}{3K_B T} \quad (7)$$

Hear, r_h is hydrodynamic diameter of water nanodroplets,k is Boltzmann's constant, T is the temperature in K, and η is the viscosity of solvent.

3.1.1. DLS measurement of AOT nano-micelles containing Rhodamine B

Fig. 2s shows a plot of the autocorrelation function versus decay time for AOT RMs containing the different concentrations of RB at the different MFDs (0.01, 0.04, 0.07, and 0.1).

It can also be seen from Fig. 2s that, the autocorrelation function of water droplets comprising various Rhodamine B concentrations and different MFDs is a single relaxation curve.

To obtain relax rate of AOT droplets, the autocorrelation function of AOT RMs was fitted with a single exponential function, and then the collective diffusion of AOT micelles was calculated using the relation (4)·[25]. The hydrodynamic radius of water nano-droplets was calculated using the Stokes-Einstein relation.

The collective diffusion coefficient and hydrodynamic diameter versus mass fraction of nano-droplet of the AOT RMs at the different concentrations of RB are shown in Figs. 1 and 2.

Fig. 1 shows that at the low Rhodamine B concentration (0.0000625), the diffusion coefficient of AOT droplets increased as a function of MFD. Upon increasing the concentration of dye, from 0.0000625 to 0.001 (high concentration) in the AOT reversed micelles, the diffusion of AOT micelles decreased with mass fraction of nano-droplet. In other words, our results indicated that the inter-droplet interactions changed from attractive to repulsive as concentration of Rhodamine B was decreased in the AOT RM system