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Photophysics of Rhodamine B in the nanosized water droplets: A concentration dependence study

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ABSTRACT

The photophysics of Rhodamine B (RB) dye at both low and high concentration was studied in confined water nanodroplets within water/AOT/n-hexane microemulsions (MEs) at constant water content as a function of mass fraction of droplet (mfd) using techniques such as Uv–Vis and fluorescence spectroscopy, as well as dynamic light scattering (DLS). The study of the diffusion coefficient of nanometer-sized water droplets by the DLS technique showed that with increasing concentration of Rhodamine B (RB) dye, the interactions between nano-droplets were altered from attractive to repulsive as a function of mass fraction of droplets increased. Uv–Vis spectroscopy showed that at high concentrations of Rhodamine B (RB) dye molecules, the absorption spectra of samples deviated from Beer's law, and is broader at larger mfd due to the interactions of RB dye molecules. The comparison of fluorescence spectra of water droplets containing RB dye at low (0.0000625) and high concentrations (0.001) showed that the fluorescence emission intensity of AOT MEs at high concentration of RB molecules quenched due to aggregation of dyes molecules, and the red shift in λ_{max} of fluorescence was observed by increasing the dye's concentration. It was also observed that changes in intensity and λ_{max} of fluorescence were most significant in a region where the mfd of the water/AOT/n-hexane MEs was relatively small, and approached an extreme at larger mfd. The stokes shift and dipole moments' ratio of ground to excited state (μ_g/μ_e) of water/AOT/n-hexane microemulsion containing Rhodamine B at a high concentration of 0.001 increased as a function of mfd, whereas at a 0.0000625 concentration, it included two slopes of mfd = 0.04, but in both concentration, they remained almost constant at larger mfds.

1. Introduction

In polar solvent-in-oil microemulsion (ME), the surfactant-capped water droplets, or polar solvent, are dispersed in a bulk non-polar solvent. In the water-in-hexane AOT ME, an outer layer of AOT surfactant molecules confines the H_2O nano-droplet with hydrophilic head groups pointing inward to the center containing nano-sized polar water droplet and the hydrophobic tails extending outward into the hexane continuous phase. Properties of the W/O AOT ME system is affected by the molar ratio of H_2O (or polar solvent)-to-surfactant that reflects the polar solvent content within nano-sized [1] and mass fractions of droplet [2], which changes by the mass of the oil, AOT, and polar solvent components.

Recently, study of water-in-oil microemulsion systems has grown considerably due to their application in mimetic agents and cell biomembranes modeling, non-reactors micelles, drug delivery, oil recovery, and enzymology, most owing to the excellent solubility of the hydrophilic compounds in the aqueous core of MEs [3]. On the other hand, the nano-scale entrapped-water is found in many physical and biological microenvironments. The confinement of nanometer-sized water pools induces different dynamics in a liquid system compared to their bulk counterparts due to the surface-to-volume effect [4–5].Water-in-oil AOT microemulsions produces nonpolar–polar interfaces and nanometer-sized locations for the water-soluble additives such as dyes. The W/O MEs influence the photo-physical properties of dyes. Red or blue shifts and intensity enhancing or self-quenching have been observed in the absorption and emissions spectra different from their bulk counterparts due to molecular interactions in the confined environment [6]. Rhodamine B is a xanthenes-based fluorescent hydrophilic dye, due to its unique photo-physical properties, it is widely used as laser dyes, fluorescence standards, fluorescent dyes to characterization of the polymer nanoparticles surface, lipid membranes fluidity, polymer-bioconjugates detection, physisorption and chemisorptions study of oligonucleotides on latexes, investigating

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structure and dynamics of micelles and single-molecule imaging, and imaging in living cells [7].

The Rhodamine B cationic dye is sensitive to its surrounding environment. Interaction of RB molecules has been reported in aqueous and other liquid media [8–12].

In literatures, photophysic of the different fluorescent dyes based on change of the non-polar bulk oil type and the molar ratio value of polar solvent to surfactant molecules have been reported in water-in-oil micro emulsion [13–19].but no data on photophysic of Rhodamine B cationic dye in the water/AOT/hexane reverse micelle systems based on the different Rhodamine B concentrations at the constant water content has been reported, to our knowledge. Therefore, In the present study, the photophysics of Rhodamine B cationic dye in the reverse microemulsion of water/AOT/n-hexane was studied at the constant water to AOT molar ratio ($W = 10$) and different mfd thus changing the RB concentration by techniques of absorption and fluorescence spectroscopy as well as dynamic light scattering (DLS) Fig. 1.

2. Experimental

2.1. Reagents

The dioctyl sodium sulfosuccinate, AOT (Sigma–Aldrich, purity >99%), n-hexane (Sigma–Aldrich, purity >95%) and Cationic dye, Rhodamine B (Sigma–Aldrich, purity >95%) with fluorometric grade were used without purification.

2.2. Preparation of loaded–Rhodamine B water nanodroplet dispersions

To prepare the AOT water nanodroplets containing different Rhodamine B concentrations, at the first, a measured amount of RB dye powder was dissolved in deionized water in terms of the certain concentration, which the mass ratio of dye-to- water was defined as concentration of the Rhodamine B dye in the Aerosol-OT RM. Then AOT reverse micro emulsions was prepared by mixing the needed mass values of the AOT surfactant, n-hexane oil and deionized water containing the different RB dye concentration based on the fixed molar ratio of water-to-AOT ($Y = 10$) and finally the system was diluted with hexane oil based on the defined mfd at room temperature (RT).

2.3. Characterization

The autocorrelation function of AOT droplets was obtained by 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 were carried out by using a UV-1650 PC spectrometer (Shimadzu) in the wavelength of 350 to 800 nm. The emission spectrum of samples at the excitation wavelength 554 nm was recorded with a Jasco FP-6200 spectrofluorimeter. The absorbance and fluorescence of the AOT RM samples were measured using a quartz cuvette.

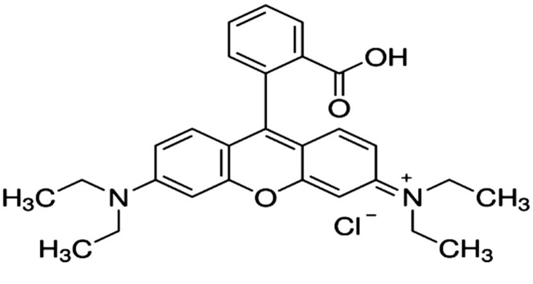

Fig. 1. Chemical structure of Rhodamine B.

3. Result and discussion

3.1. Dynamic light scattering measurement

Dynamic light scattering (DLS) is a valuable instrument to study the interaction between nanometer-sized water droplets using diffusion coefficient and to characterize the size distribution of droplets by a digital correlate, which utilizes the time autocorrelation function in analyzing the modulation of the scattered light intensity that passes through a solution containing nanosized-scale droplets. In DLS experiments, time-dependent fluctuations of scattered light intensity due to the Brownian motion of nano-sized water droplets were measured. The normalized field autocorrelation function, $g^1(\tau)$, was derived from the scattered intensity of the Siegert relation for a given delay time τ, and is given by [20–22].

$$g^1(q,\tau) = \left(1 - \frac{\langle I(q,t)I(q,t+\tau)\rangle}{\langle I(q,t)\rangle^2}\right)^{1/2} \tag{1}$$

where $I(q, t)$ and $I(q, t + \tau)$ are the scattered light intensities at times t and $t + \tau$, respectively.

In dilute monodisperse colloidal solutions, function of $g^1(q, \tau)$ is [20–26]:

$$g^1(\tau) = A\exp(-\Gamma\tau) \tag{2}$$

where A is an instrumental constant. A decrease in particle sizes results in faster exponential decay with a larger decay constant, as the fluctuations in light intensity changes more rapidly; whereas for larger particles, a slowly decaying exponential plot is realized with a small decay constant. Therefore, the decay rate is inversely proportional to particle size [20–24]. The relaxation rate, Γ, is related to the collective diffusion coefficient, Dc, based on [20–24]:

$$D = \Gamma/q^2 \tag{3}$$

where q is the scattering vector [20–24]

$$q = \frac{4\pi n}{\lambda}\sin\left(\frac{\theta}{2}\right) \tag{4}$$

where n is the refractive index of the non-polar solvent, λ is the wavelength of the laser and θ is the scattering angle [20–24].

The diffusion coefficient is converted to the hydrodynamic radius by using the Stokes-Einstein relation [20–24]:

$$r_h = \frac{K_B T}{6\eta\pi D} \tag{5}$$

where T is the temperature in K, η is the viscosity of continuous phase and K_B is Boltzmann's constant.

The reorientation time (τ_r) for spherical nano-sized water droplets containing RB in AOT ME were obtained by using the Stokes-Einstein-Debye (SED) hydrodynamic model [23–24].

$$\tau_r = \frac{4\pi\eta {r_h}^3}{3K_B T} \tag{6}$$

Here, 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.

In this study, for dynamic analyses of nano-scale water droplets containing different RB concentrations in the water/AOT/n-hexane MEs, the autocorrelation function was constructed using the DLS technique. The autocorrelation function vs. decay time for AOT ME containing multiple RB concentrations at mfd = 0.01, 0.04, 0.07, and 0.1 is presented in Fig. 2.